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PROCEEDINGS

Joint Conference on Prevention and Control of Oil Spills

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27 Abstract

On December 15-17, 1969, a Joint Conference on Prevention and Control of Oil Spills was held under the cosponsorship of the American Petroleum Institute and the Federal Water Pollution Control Administration. The objectives of the conference were to delineate the overall dimensions of the oil spills problem, explore the present state of the art of prevention and control of oil spills, and review the relevant research and development efforts of government and private industry, both here and abroad. The topics discussed include spill prevention, boom design, mechanical removal, chemical additives, analysis and sampling, monitoring, beach cleanup, fate of spills, ecological effects, and oil-spill information retrieval and dissemination. (Knapp-USGS)

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PROCEEDINGS

Joint Conference
on
Prevention and Control
of
Oil Spills

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Joint Conference on Prevention and Control of Oil Spills

sponsored by

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and
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FOREWORD

On December 15-17, 1969, a Joint Conference on Prevention and Control of Oil Spills was held under the cosponsorship of the American Petroleum Institute and the Federal Water Pollution Control Administration at the Americana Hotel, New York City.

The objectives of the conference, which attracted an international audience of some 1,100, were to delineate the overall dimensions of the oil spills problem, explore the present state of the art of prevention and control of oil spills, and review the relevant research and development efforts of government and private industry, both here and abroad.

All technical papers and major addresses presented at luncheon and dinner sessions are included in their entirety in this volume. Because of time limitations during the conference, most authors presented only a summary of their complete paper.

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OPENING SESSION

Monday, December 15, 9:00 a.m.

Chairman: Kerryn King
Vice President, Texaco Inc.

Chairman, Committee for Air
and Water Conservation
American Petroleum Institute

Co-Chairman: L.P. Haxby
Shell Development Company

Chairman, Subcommittee on Oil Spills Cleanup
American Petroleum Institute

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Opening Remarks

Kerryn King
Vice President, Texaco Inc.

and

Chairman, Committee for Air and Water Conservation
American Petroleum Institute

On behalf of the American Petroleum Institute and the Federal Water Pollution Control Administration, it is my pleasure to welcome you to this joint Conference.

We are, of course, pleased that this Conference has attracted such widespread interest. With us are people from all across the United States—and around the world. Our foreign visitors—who come from five continents—comprise roughly 10 per cent of the Conference registration. Here, together, are businessmen, representatives of many governments, conservationists, members of citizen groups, academicians. It is a clear demonstration of today's universal concern not just about the oil spills problem, but the total environment of today's world.

Once man was willing to let the environment absorb pollutants as part of the cost of the goods and services he wanted. And it really didn't seem to matter, because the ability of our air and water to assimilate waste seemed almost unlimited. But today we have come to realize—as our population and our demands grow—that our environment is threatened by our very way of life. This does not mean that growth and environmental quality are incompatible. It simply means that we are going to have to assure that our environment is not required to absorb an inordinate part of the true cost of the goods and services our population demands. We are going to have to pay the full cost of production to avoid severe and, in some cases, permanent environmental damage.

There is no escaping the fact that the cost of environmental conservation will be high. We will be required to allocate an ever-increasing share of our economic resources to it.

But conservation of our environment doesn't mean that it cannot continue to be used for man's welfare. As our population continues to grow, the job of feeding, clothing, housing, educating, transporting, and providing for the other physical needs of human beings will be staggering. Our environmental resources will be put to heavy use—but they will have to be used wisely.

We in the petroleum industry are in the business of converting a valuable natural resource into a myriad of products—primarily energy—to meet man's needs. We have long dedicated ourselves to the cause of true conservation, which is use without abuse.

Being among those who *meet* society's demands, we share with those who *make* the demands an obligation to see that they are met with the least possible harm to the environment. In recognition of this shared responsibility, we and others in industry—*meeters* of demand—seek to join our conservation efforts with government—which represents the people, the *makers* of demand.

My industry—through API—for some time has sponsored a broad program of environmental research, and much of it has been research conducted with the Federal Government and other industries. During 1970 we estimate that at least half of our API conservation research expenditures will go into such jointly sponsored projects. And most of these projects will be conducted with the Federal Government.

It is this same kind of cooperation that has made this Conference possible. This is the result of a joint commitment—a commitment to do something about a real problem that none of us can solve alone.

None of us is here to defend past performance or simply to declare our good intentions for the future. We *are* here to discuss seriously, in a technical and scientific forum, what concrete things we can do, now and in the future, to reduce the hazard of oil spill damage to the environment. More specifically, our objectives are:

1. To review the present state of the art of oil spill prevention and control.
2. To review present research efforts aimed at advancing the state of the art, including those efforts being made by government, the academic world, and industry.
3. To determine what additional efforts are needed and what directions they should properly take.

These are ambitious objectives, but nowhere before has a better qualified group of experts assembled to pursue them. We have with us many of the key people, from both government and industry, who were on the scene during the *Torrey Canyon* and Santa Barbara cleanup operations. We have marine biologists who have closely studied the effects of both those incidents. And we have representatives of many of the leading research organizations engaged in developing new and more effective systems for controlling oil on water.

Hopefully, over the next two and one-half days, the broad dialogue that will be established will lay the foundation for a continuing fruitful exchange of information, ideas, and viewpoints among all those concerned with the oil spills problem.

There are many millions of our fellow citizens deeply concerned about the topic we will discuss. I know I share your conviction that we will and we must find new and better answers to help assure the future of this planet. As of right now, it's the only one we've got!

A History Of Major Oil Spill Incidents

K.E. Biglane
Director, Division of Technical Support
Federal Water Pollution Control Administration
Washington, D.C.

Abstract

This paper summarizes some of the major oil spills of recent years and discusses some of the causes of these spills and their effects on the environment. Information is presented on research needed to control oil spills and on domestic and international legislation needed to provide compensation for oil pollution damage.

In 1907, the tanker, *Thomas W. Lawson*, crashed into the Isles of Scilly and lost her total cargo of two million gallons of crude oil. In 1967, the tanker, *Torrey Canyon*, crashed into the Seven Stones Rocks, a reef between the Isles of Scilly and the coast of southwestern England and she lost a cargo of over 30 million gallons of crude oil. Both tankers were responsible for oil pollution of the sea and shorefaces. The *Torrey Canyon*, however, resulted in an almost unbelievable spread of oil pollution to the territorial seas and other properties of two nations. For this, the *Torrey Canyon* casualty will neither be easily forgotten nor casually dismissed by the world's maritime industry or world governments.

The title of this paper suggests that the display of a long and detailed historical and projected chronicle of significant spills of oil to the environment would quite properly set the stage for this jointly sponsored industry/government Conference. However, as both industry and government are acutely aware, not one more spill entry is needed to further justify the demands, by all concerned, that such episodes be prevented or swiftly controlled.

Before 1967, the year of the *Torrey Canyon*, an oil spill episode did not engender the same widespread public impact on the world's community that it does today. Then, the impact was confined generally to a small but vocal group of conservationists in concert with a few industrial and governmental pollution control organizations. For example, what is now commonly referred to as an oil blowout used to be termed a "gusher" and this event signaled almost boundless wealth for the petroleum prospector who was often pictured happily bathing in a crude oil shower. Such was the case in March 1910 when the famous Lakeview gusher in the Midway-Sunset Field, California, spewed an estimated 8.25 million barrels of oil before it died some 18 months later. History records that over one-half of this oil was collected and saved in 20 earthen reservoirs covering a 60-acre area. Later, as oil and gas blowouts increased in the oil drilling business, a new breed of man arose to fight and conquer the uncontrolled, sometimes flaming wells and an admiring public found excitement in hearing of these risky exploits.

By the same token the report of a non-wartime tanker casualty before 1967 stirred little or no public reaction except on those occasions when hapless seamen lost their lives by fire or were drowned. Distraught vessel owners and insurors grimly accepted their losses and some of the world governments began to meet and further discuss safety of life at sea, ship construction standards, rules of the road, and crew competency.

As was noted in the document, "Oil Pollution–A report to the President," the maritime casualty rate, including vessels on inland waters, remains sufficiently high to justify serious concern. For the two fiscal year periods 1966-67, there were a total of 3,200 vessel casualties of all types reported in United States waters and 1,507 casualties reported elsewhere. The Corps of Engineers estimated that there were 2,000 oil spills in United States waters in 1966, and the U. S. Coast Guard recently estimated that we may be experiencing a spillage of polluting materials to United States waters approaching 10,000 incidents annually, with oil leading all other categories by a ratio of about three to one.

If the *Torrey Canyon* in 1967 heralded the onset of super spills from a single tanker casualty, then the year 1968 did its best to produce spills from multiple tanker groundings and sinkings. In that year, at least seven tankers, the *Tank Countess* off Norway; the *General Colocotronis* off the Bahamas; the *Ocean Eagle,* off Puerto Rico; the *Esso Essen,* the *Andron,* and the *Sevilla,* off South Africa; and, the *Witwater,* off Panama, lost a total of 16 million gallons of crude and fuel oils to the oceans. Even though this combined loss represented about one-half the cargo carried by the *Torrey Canyon,* widespread pollutional damages suffered by coastal states as the result of maritime casualties were decidedly on the increase.

Although a tanker casualty can result in a pollution spectacular, the period of danger to marine life and shore property is relatively short-lived. The restoration of damaged property and the re-population of affected biota usually begins within a short time following the casualty. Not so, however, in those environments in close proximity to some of the world's heavily trafficked sea routes. Continuing discharges of oil contained in tank washings, bilges, and de-ballasting operations also fall under the definition of "oil spills" but the effects on the marine ecosystem are incipient, chronic, and debilitating. Like effects are noted also in fresh water environs receiving daily dosings of untreated industrial and municipal wastes.

As in all cases where man poses, by polluting, additional perils to resident life on this planet, certain life forms show an immediate reaction and their populations are severely curtailed to the point of near extinction. For instance, waterfowl are particularly susceptible to oil pollution and ornithologists have noted, since the early 1900's, the appalling loss of seabirds world-wide and the disappearance of all breeding colonies of certain species in chronically oil polluted coastal areas such as Kent and Sussex in England and in Normandy, France.

This history of oil spills incidents is by no means complete. The chronicle will be expanded in other papers at this seminar. Some of the now famous incidents such as the *Torrey Canyon* and the Santa Barbara blowout will be explored further by the seminar. The loss in October of this year of about eight million gallons of crude oil from a storage tank at Sewaren, New Jersey, to a tributary of Raritan Bay and the breaking up of an oil tanker several hundred miles off the eastern coast of the United States and another off of Taiwan, both in November of this year and both resulting in loss of seamen, apparently, did not result in widespread oil pollution damages to the environment. However, each incident added to the growing concern over such episodes.

Because of the apparent increase in the number of maritime casualties in the past few years, coupled with the growing number of carriers in the super tanker category, oil pollution control research and domestic and international legislation designed to prevent and to compensate for expensive oil pollution damages has also been stimulated. Most of us are quite familiar with the oil pollution control measures proposed by both the House of Representatives and Senate in the U. S. Congress. As of this writing, both legislative proposals have passed their respective houses and are being discussed in a joint conference to decide on a final measure acceptable to the Congress as a whole.

The Secretary of the Department of the Interior issued strict new operating and leasing regulations in August of this year for mineral development on the Outer Continental Shelf. These new regulations were strengthened to prevent and control pollution from such operations. Also, the Secretary has ordered the National Multi-agency Oil and Hazardous Materials Plan to be strengthened. The revisions to the Plan are nearly complete and will be discussed further in another paper.

New international agreements are in the offing for the protection of the rights of coastal states to intervene when they are affected by maritime casualties on the high seas; for the provision of civil liability for oil pollution damage; and, to expand the scope of existing anti-pollution actions to other hazardous and toxic materials.

In summary, this joint meeting is timely and, should be of immediate value to those in government and industry who seek to prevent and, that failing, to immediately control spills of oil to the aquatic environment. After nearly three years since the *Torrey Canyon* casualty, this Nation–and I suspect this is true worldwide–still cannot mount sufficient technical or operational responses to positively control large spills of oil once it has been spilled to the aquatic environment. I say "positively control" because if the spill is forced onto the shorelines and despoils shore-based property, contaminates and destroys living marine resources, imposes hazards to the health and welfare of coastal residents, or impairs any other facet of the ecosystem, then overall control gives way to assignments of particular priorities for protection. This is usually followed by a priority restoration of that which has been damaged. It may be that this will be the case for quite some time to come.

A word of caution–based on the history of oil spills–is needed here. Some would have the public and others believe that a single technique or system, applied to either the control or the clean-up of spills, is the ultimate goal in this problem area. Those of us in the Federal Water Pollution Control Administration do not happen to share this view and we are recommending that we continue to concentrate our research and operational efforts along the lines of multiple system responses as opposed to single system panaceas. History will record whether we are right . . . or wrong.

National Multiagency Oil And Hazardous Materials Pollution Contingency Plan

John R. Hyland
Acting Chief, Special Control Programs Branch
Division of Technical Support
Federal Water Pollution Control Administration

Abstract

The National Multiagency Contingency Plan, prepared at the Direction of the President, provides a mechanism for coordinating the Federal response to a spill of oil or other hazardous materials. Agencies signatory to the Plan are: Department of the Interior; Department of Transportation; Department of Defense; Department of Health, Education and Welfare; and Office of Emergency Preparedness. The objectives of this Plan are: to develop appropriate preventive and preparedness measures and effective systems for discovering and reporting the existence of a pollution spill; to institute, promptly, measures to restrict the further spread of the pollutant; to assure that the public health and welfare are provided adequate protection; to apply techniques to cleanup and dispose of the collected pollutants; and to institute actions to recover cleanup costs and to effect enforcement of existing Federal statutes. The Plan is effective for all United States navigable waters and contiguous zone. The President has established the policy that appropriate Federal resources will be used for dealing with the pollution aspects of oil or hazardous substance spill problems and to protect our natural resources from their consequences. A primary thrust of regional plans is to encourage the person responsible for the discharge of oil or other hazardous substances to remove the pollutant or adequately mitigate its effects. The National Response Team (NRT) consists of representatives of the signatory agencies and acts as an emergency response team to be activated in the event of a pollution incident involving oil or other hazardous materials. The Regional Response Center (RRC) is the regional headquarters site for pollution control activities under this Plan. Coordination and direction of Federal pollution control efforts at the scene of a pollution incident is accomplished through an On-Scene Commander (OSC). The OSC is the single executive agent predesignated by the regional plan to coordinate and direct such pollution control activities in each area of the region. The actions taken to respond to a spill or pollution incident can be separated into five relatively distinct phases.

For descriptive purposes these are: Phase I. Discovery and Notification; Phase II. Containment and Countermeasures; Phase III. Cleanup and Disposal; Phase IV. Restoration; and Phase V. Recovery of Damages and Enforcement.

My assigned task here is to explain to you the National Multiagency Oil and Hazardous Materials Pollution Contingency Plan. But allow me to digress from that if you will and with a brief explanation of the Plan itself, give you some of the examples of spills, how they were handled and some of the results of the operation of the Plan.

As a result of increased concern and growing public awareness of the number of accidental spills polluting the Nation's waters, the President of the United States directed that a study be made of how the Nation's resources could best be mobilized, an assessment of existing resources and recommendations for an effective national program.

The report responding to the President's directive, "Oil Pollution – A Report to the President", was published in February 1968. It contained the recommendation for a National Plan to deal with these problems.

In September 1968, the five Federal agencies most concerned with oil pollution–Interior; Transportation; Defense; Health, Education and Welfare; and the Office of Emergency Preparedness, completed preparation of a National Contingency Plan. The effort to prepare and publish the Plan was led and chaired by the Department of the Interior.

The Plan was completed, agreed to by the agencies involved, signed by the respective heads of the agencies and placed in effect by the President in November 1968.

The National Multiagency Contingency Plan, prepared at the request of the President, provides a mechanism for coordinating the Federal response to a spill of oil or other hazardous material. The objectives of this Plan are: to develop appropriate preventive and preparedness measures and effective systems for discovering and reporting the existence of a pollution spill; to institute, promptly, measures to restrict the further spread of the pollutant; to assure that the public health and welfare are provided adequate protection; to apply techniques to cleanup and dispose of the collected pollutants; and to institute actions to recover cleanup costs and to effect enforcement of existing Federal statutes. The Plan is effective for all United States navigable waters and contiguous zone. The President has established the policy that appropriate Federal resources will be used for dealing with the pollution aspects of oil or hazardous substance spill problems and to protect our natural resources from the consequences. A primary thrust of regional plans is to encourage the person responsible for the discharge of oil or other hazardous substances to remove the pollutant or adequately mitigate its effects. The National Response Team (NRT) consists of representatives of the signatory agencies and acts as an emergency response team to be activated in the event of a pollution incident involving oil or other hazardous materials. The Regional Response Center (RRC) is the regional headquarters site for pollution control activities under this Plan. Coordination and direction of Federal pollution control efforts at the scene of a pollution incident is accomplished through an On-Scene Commander (OSC). The OSC is the single executive agent predesignated by the regional plan to coordinate and direct such pollution control activities in each area of the region. The actions taken to respond to a spill or pollution incident can be separated into five relatively distinct phases.

These are:

1. Discovery and notification;
2. Containment and countermeasures;
3. Cleanup and disposal of the pollutant;
4. Restoration of the environment;
5. Recovery of damages and enforcement, as required in each case.

The individual agency responsibilities under the Plan (and these can be concurrent at any phase of the plan) are: Interior administers and revises the National Plan and develops and revises Regional Plans. The Department of the Interior also provides technical expertise relative to pollution control techniques for spills of both oil and hazardous materials.

The Department of Transportation supplies the OSC with expertise in navigation, port safety and maritime law enforcement.

The Department of Defense may provide assistance in critical pollution incidents and consistent with its basic operational requirements.

The Department of Health, Education and Welfare is responsible for providing expert advice and assistance in those pollution incidents that constitute an immediate threat to public health.

The Office of Emergency Preparedness (OEP) maintains an awareness of pollution incidents as they develop. If a major disaster is declared, then the Director of the Office of Emergency Preparedness provides coordination and direction of the Federal response in accordance with OEP policies and procedures.

Use of the Plan during the Santa Barbara incident resulted in the Regional Team being activated. The National Team, while on a constant alert, was not activated because the Regional Team was able to control responses to the incident.

The Plan is now undergoing some revision to better define and more exactly reflect agency responsibilities. Additionally, annexes are being considered and proposed to the Plan. These include a model regional plan and are in for consideration only at this time.

But how has use of the Plan worked? Let me give some recent examples of this.

One pollution incident, reported by our Great Lakes Region, occurred earlier this year on July 14, 1969, at Wood River, Illinois, along the Mississippi River, where the river crested at an elevation of 425 feet above Mean Sea Level (MSL), the highest flood stage in eighteen years.

American Oil Company's (AMOCO) refinery complex there is protected by a flood levee, constructed to an elevation of 442 feet MSL, suitable for a 200 year flood. The company has a series of eight oxidation ponds located on the riverside of the levee in an area subject to flooding. Before refinery effluent is discharged to the Mississippi River, it passes through gravity-type oil separators which are located inside the refinery proper. Oil which is not removed by separators and reaches the oxidation pond is skimmed off the surface of the last two ponds and pumped back for refining. Approximately 20 bbl/day of oil is discharged to the oxidation ponds.

This summer the dike was raised an additional three feet. However, due to the topography and a higher flood stage than was earlier predicted, floodwaters flowed northward into the area of the oxidation ponds and flushed the oil out of the ponds. On July 14 the Federal Water Pollution Control Administration, Great Lakes Regional Office along with the Corps of Engineers, received notification from the Coast Guard, St. Louis, for assistance in directing a containment and cleanup operation to prevent additional pollution of the Mississippi River.

The initial survey made by the Regional Team indicated two vacuum pumping trucks, similar to the type used in oil storage tank cleaning operations, removing oil near the bank at a slow rate. Approximately 1,250 feet of boom were in place. Some oil was observed to be flowing off of AMOCO's property and into the Mississippi River. Fortunately the wind was out of the east and concentrated most of the oil in and along the road. Had the road which parallels the river not been elevated, the oil would have had direct access to the Mississippi River in the vicinity of the heavy oils dock. There was a danger that the wind might shift to the west and allow oil to flow back into the river with the receding floodwaters.

Recommendations placed in effect to prevent further pollution included the use of straw and additional booms. AMOCO personnel had started construction of a secondary dike built at right angles to the roadway from west to east.

Federal Water Pollution Control Administration (FWPCA) representatives were asked if chemicals might be used in dispersing the oil. We replied that our chemical policy allowed the use only under certain conditions and that the situation here did not warrant the use of chemicals. Furthermore, the problem of toxicity must be considered. Although research has indicated that some dispersants are far less toxic by themselves, the emulsions formed by the dispersants have been proven to be highly toxic. Also, the effects of emulsions must be considered not only on the flora and fauna but also on the water entering municipal water intakes. Most of the St. Louis water supply is taken from the nearby Chain of Rocks pumping station.

FWPCA officials recommended that the oil be *physically* removed with the use of straw. At the time, AMOCO, along with some of the government officials, were skeptical about the absorptive capacity of straw since the oil was of a heavy nature. We indicated that straw had been successfully employed in the past and that it is more suited to improvision for removal than other materials.

AMOCO officials stated they were having trouble getting straw. It was suggested that, if necessary, AMOCO should ask local farmers and elevator concerns to supply the necessary straw. In the early evening hours, a supplier of straw was found and AMOCO made arrangements to have it delivered. That evening AMOCO brought out floodlights and began around-the-clock operations.

Additional sections of boom were moved into the north area so as to confine pockets of oil which had concentrated there. It was also suggested that straw be placed in various areas outside the present confinement areas and that laborers be utilized to pick up pockets of straw and oil. Before FWPCA officials left the scene late Tuesday afternoon, they observed straw being placed in the suggested areas and laborers being assigned to pick up oil in those areas.

During the cleanup operation, suction trucks, bulldozers, tractors, small boats, and trucks were being utilized. A crane was also used to pick up oil-soaked straw and debris in areas away from the shoreline. Rakes were used to pull residual amounts of oil-soaked straw onto the banks to be trucked away for disposal. Within one and one-half days, a considerable amount of oil had been removed, estimates varying from 60 to 80 percent. Oil that remained was completely encircled and there was little danger of it being discharged into the Mississippi River in the event that the wind shifted unfavorably.

By Thursday afternoon, three days later, the cleanup operations were just about completed and the water level had fallen so that the oil remaining was now behind diked areas. By Friday, the river had dropped to 31.9 feet, four feet below the flood crest. The upper end of the oxidation ponds were now protected by the dike in the area. The area where there had been a heavy concentration of oil was now no longer submerged. (This was the first high water since the oxidation ponds were put in [1957] according to an AMOCO official.) The river was expected to drop an additional 2-½ feet by Saturday morning. Cleanup operations were concluded.

Conclusions and recommendations made as a result of this operation were:

1. Facts support a violation of U. S. River and Harbor Act of 1899.
2. Lack of adequate safeguards to prevent contents of ponds from entering the river. AMOCO waste pond facility vulnerable to flooding. Other area industrial facilities also vulnerable. Joint inspection of area by FWPCA, U. S. Army Engineers, Coast Guard, and Illinois Sanitary Water Board needed in order to make recommendations to industry for the prevention of future pollution incidents.
3. AMOCO allowed area to be used as trash dump which during flooding would present navigation problems.
4. Straw was most effective in the removal of oil.
5. Skimming boat vulnerable to mechanical failure.
6. AMOCO was most cooperative in following federal officials' suggested containment and cleanup procedures.
7. FWPCA, U. S. Coast Guard and Corps of Engineers have a good close working relationship in the St. Louis area.
8. Industry needs to accept more responsibility in the *prevention* of pollutional incidents.
9. Oil covered some vegetation in the southern area of AMOCO's facility. Subsequent rain may flush some of this oil out. No possible way of picking up this oil in present location.
10. Oil coated parts of the levee.

Another example of a spill, this one involving hazardous material, occurred at Dunreith, Indiana, January 2, 1969. A train wreck there caused the derailment of tank cars containing chemicals. Among the cars derailed, one containing cyanohydrin, ruptured, spilling 20,000 gallons of the chemical onto the ground. This is equivalent to approximately 47,000 pounds of cyanide. About 1,200 gallons reached Buck Creek there in the area, endangering a downstream water supply and killing all the fish in the locale of the spill. A chemical neitralizer was added to the stream to remove the cyanide and FWPCA personnel assisted in analyzing water samples to assure that public water supplies were safe to use before being put back in service. The FWPCA laboratory at Evansville, Indiana, was on alert from the first notice of the disaster and was prepared to lend assistance as needed.

More recently on a Thursday afternoon, October 30, 1969, at Sewaren, New Jersey, along the Arthur Kill, an

8.4 million gallon storage tank for crude oil failed. The resulting wave of oil flowed over the surrounding ten foot dike and spread on down the drainage, some of it eventually reaching Raritan Bay. The Contingency Plan was immediately placed in effect and within hours of the report, teams were present and on the scene. The Coast Guard provided the on-scene direction and FWPCA provided pollution abatement advice and technical assistance. The following day aerial reconnaissance and photography was accomplished and by four o'clock that afternoon, the extent of the pollution was fully known. The crude oil had spread over the tank storage area, into a settling pond and on down Smith Creek, into the Arthur Kill and Raritan Bay. An estimated million gallons of oil escaped the immediate area into the surrounding water environment.

Containment and cleanup were handled by regional personnel. Facilities and equipment utilized included: 15 vacuum trucks, 3 straw booms, 2 absorbent booms and a minor amount of chemical dispersant.

In summary then, with an estimated 800 to 1000 of these type spills a year, an operable contingency plan is needed to respond to these kinds of spills. Two of the examples involved retaining dikes and one common feature of these structures is that there are no overall regulations for design or structural requirements. The other example involved transportation facilities. These problems should give us an awareness of the preventative steps needed to protect the environment.

Mother nature does not operate here in these kinds of polluting incidents as she might with some lightly degraded streams—such that restore themselves in a few miles of tumbling flow; when it comes to these kinds of polluting spills we would do well to not let history write that we passed by on the other side and remind ourselves again that, "here on earth God's work must truly be our own."

Acknowledgments

The report and photographs of the Wood River, Illinois, incident of July 14, 1969, were provided by Mr. James A. Pappas, Great Lakes Basin Region, FWPCA. The photographs of the oil spill on October 30, 1969, at Sewaren were taken by Mr. Richard Tatlock, Coastal Research Corporation, Boston, Massachusetts. I am also indebted to Mr. Kenneth E. Biglane, Director, Division of Technical Support, FWPCA, for his review and suggestions, particularly with regards to the history and review of the Plan.

Industry Research And Response Plans

L. P. Haxby
Manager, Air and Water Conservation
Shell Development Company

and

Chairman, Subcommittee on Oil Spills Cleanup
American Petroleum Institute

My purpose here today will be to review briefly the history of the American Petroleum Institute's efforts at oil spills control and to describe our present programs and plans.

Until recently, oil pollution was looked upon mostly as a problem associated with tanker operations, particularly the disposal of oily ballast and tank washings, which were once routinely discharged at sea. Over the years, this problem has largely been brought under control by improvements in tanker operations, such as the "load on top" method of retaining oily residues on board for disposal in proper facilities ashore. The industry is justifiably proud of its progress in eliminating this type of pollution.

Again until recently, accidents at sea had caused occasional incidents of oil pollution, but such incidents fortunately had been relatively few. The marine segment of the petroleum industry was quick to point out–again with some justification–that its overall safety record had been excellent.

Then, of course, came the *Torrey Canyon*. Almost immediately, as the stories of the devastation of the Cornish and French coastlines reached this country, people in coastal areas began to ask, "Can it happen here?" Suddenly, even small, accidental spills at terminals in rivers and harbors began to command headline attention, and the attention of our industry. President Johnson called for an interdepartmental study and for the preparation of a national contingency plan.

API's Committee for Air and Water Conservation had been concerned with the problem of oil pollution since its formation. But it is fair to say that few people, if any, foresaw the need to develop the capability to deal with oil spills of such magnitude as the *Torrey Canyon*.

It had been recognized that there was a hazard of smaller oil spills at harbors and along waterways where the petroleum industry and others operate terminals. Over two years ago, API urged its member companies to band together where possible and form local cooperatives, organizations similar to volunteer fire departments, to contain and clean up oil spills whenever they occur.

These cooperatives–of which there now are some 50–will be described later on in the program, so I won't go into detail. But, briefly, they are programs in which companies pool resources, sometimes jointly buying equipment, and establish contingency plans in cooperation with local harbor authorities, fire departments, and Coast Guard officials.

Equipment includes such things as floating booms for containing a spill, appropriate chemicals, spraying equipment, pumps, boats, and so on. Clear lines of communication are established, so that the cooperative can act swiftly and effectively in an emergency.

While these cooperative organizations can and do provide an answer to the problem of the smaller spill, we all recognize that present technology for handling large spills especially in the open sea is, to say the least, primitive.

Perhaps the most effective technique used to date was to spread straw as an absorbent and pick it up with rakes and pitchforks, as was done out in Santa Barbara. In an age when we can reach the moon, we should be able to do better than this. The question is really one of whether we are willing to commit the necessary resources of money and scientific skill to get the job done.

In February of this year, within a matter of weeks after the blowout in Santa Barbara, the API Committee for Air and Water Conservation held a special meeting to discuss the whole spectrum of issues attendant to the oil pollution problem. Industry personnel with a wide variety of backgrounds were in attendance and were asked for suggestions concerning how the industry might marshall its resources to deal with the problem.

As a result of the meeting, an existing small task force on oil spill cleanup was replaced by a permanent Subcommittee on Oil Spills Cleanup, which was charged with developing a program for action. The new subcommittee, which held its organization meeting in early April, has representatives of the production, refining, and transportation segments of the industry, as well as conservation, legal, insurance, and public relations personnel.

The API Board of Directors has thus far appropriated \$1.2 million to fund the work of the subcommittee through 1970. Most of this money will go for research and development on new methods of cleanup.

There are four task groups reporting to the new subcommittee, each dealing with a separate aspect of the problem.

The first of these is the Task Force on Equipment and Materials. This group has the assignment of studying available oil spill cleanup equipment and methods and, where needed, promoting the development of new equipment. One of its projects is the development of two sets of mathematical expressions—one to describe the rate and mechanism of the spread of oil on water under various conditions, and another to describe the various stresses that floating booms in the open sea must be designed to withstand.

Once this project is complete, work will begin on another project, which will consist first of the design and testing of scale model containment devices and finally of full-scale tests at sea.

Traditionally, oil containment booms have consisted of a tubular floating section with a weighted skirt of some kind. Such booms have proved effective in sheltered waters, but they are totally unsatisfactory under many conditions. In the open sea, booms are difficult to anchor, and wave action simply carries the oil under or over them—if they don't break apart under the wave action. We hope to solve some of these problems.

A major project of the Equipment and Materials Task Force is to develop an effective total system for containing, recovering, and storing oil spilled in the open sea or other rough water. The emphasis here is on highly flexible equipment that will be effective in up to twelve-foot waves and in winds of up to 40 miles per hour. Another design requirement is that the system be readily transportable, so that it can be moved to the scene of an accident quickly. The contract for this project, which will include design, fabrication, assembly, and full-scale tests at sea, is to be awarded shortly.

Three other projects involve agents for treating oil spills, such as sorbent materials, sinking agents, combustion aids, dispersants, and biological agents. One of these is the compilation, in a single volume, of a compendium listing all available treating agents, and giving information on the manufacturer's recommendations, availability, cost, physical properties, and so on. This project is underway at Battelle Memorial Institute. Review of the final report is due to take place in January 1970.

It is planned to develop standard testing procedures for each general type of treating agent so that comparisons of effectiveness and limitations can be made by anyone wishing to do so. This work will also be carried out at Battelle, and we hope that it can be completed in early 1970.

Another project, being carried out at Arthur D. Little, will be to determine where various types of treating agents can best be put to use, taking into account such factors as geographic location with respect to recreation and fishing areas, water conditions, local flora and fauna, and legal restraints. We are also looking for a report on this project in January.

The ultimate objects of all these studies on treating agents will be to determine their proper role in an overall response plan for coping with oil spills. Work on this plan is already going forward under another task force, as I'll explain in a moment.

The petroleum industry has, of course, been very much aware of the research efforts of the federal government—both on treating agents and on cleanup devices. I think we all recognize the need to avoid duplication of effort through an open exchange of information on technical problems.

Toward this end, the API Oil Spills Subcommittee also has a Task Force on Government Liaison, which, of course, played an important role in the planning of this joint conference. This group also does its best to stay abreast of the oil spills research being conducted by FWPCA, the Coast Guard, the Navy, the Army Corp of Engineers, and so on. It also follows the work of the Institute of Petroleum in Great Britain, as well as that of individual petroleum companies in this country and abroad.

A third task force, on Liability and Indemnification, is reviewing the many legal and insurance problems associated with oil spill cleanup. It is studying the applicability of existing insurance plans to both onshore and offshore installations, seeking answers to such questions as:

1. What insurance plans are now available and what types of oil cleanup costs are now insurable under those plans?
2. Can the industry develop an insurance scheme of its own to cover cleanup costs?
3. What liabilities does a company assume when it voluntarily assists another company in cleaning up an oil spill?

The marine transportation segment of the oil industry already has come to grips with such problems through a voluntary international indemnification plan, known as TOVALOP—which stands for "Tanker Owners Voluntary Agreement Concerning Liability for Oil Pollution." Under the plan, participating tanker owners accept, as a contractual obligation, responsibility to reimburse any national government for the costs it incurs in cleaning up oil spills they negligently cause. More than half of the Free World's tanker tonnage is now enrolled in the plan, which provides up to ten million dollars per incident per vessel, or one hundred dollars per gross registered ton of vessel capacity, whichever is smaller.

Our Liability and Indemnification Task Force will be investigating the possibility of developing an equally sound insurance plan for spills from other sources, such as offshore drilling platforms, refineries, pipelines, or terminals. The exact nature of any such scheme will have to depend, however, on the outcome of present federal legislative proposals concerning liability.

The final task force reporting to the API Oil Spills Subcommittee is charged with the development of response plans. A top-priority project of this task force, mentioned earlier, is the development of an industry response plan for massive oil spills at sea, making use of the best technology currently available.

The heart of this project is a systems analysis of present oil cleanup procedure capability. Its objective is to come up with a recommendation for an overall cleanup plan for a major spill, one of 2,000 barrels or more, that can be put into effect immediately, with existing equipment and materials.

The work has been contracted out to the Dillingham Corporation of La Jolla, California, which is attacking the problems in several phases. The first phase, now nearing completion, is a definition of the variables that must be taken into account in the systems analysis. After that will come other studies leading to the development of the final response plan itself, which will be under committee consideration in the first quarter of 1970.

A number of the other research projects being overseen by the Equipment and Materials Task Force will provide input to the Dillingham work.

The Response Plans Task Force has already completed one of its major projects, which was the preparation of a model contingency plan for individual oil company use. This model plan has been distributed to all API member companies. The model is not a detailed set of instructions, but a set of guidelines that can be useful to an oil company in developing a plan of its own.

The Response Plans Task Force is studying the petroleum industry's overall in-house capability. One of its activities is an inventory of all oil industry installations on or near bodies of water to determine the present status of preparedness to deal with oil spills.

We hope to determine what equipment is available, as well as where it is located. We also will be attempting to assess the risk of an accident's happening at various locations, what products are likely to be involved, and where outside assistance can be obtained. Once weak spots have been pinpointed, remedial measures can be taken. It is hoped, for example, that this project will reveal those areas where further cooperative arrangements among oil companies should be developed.

The Response Plans group is also inventorying and evaluating so-called "third-party services"–independent contractors with special skills and equipment who can assist in cleaning up oil spills.

Stimulating the development of a brand-new technology and implementation of contingency plans on a broad scale may not be easy objectives to reach, but I believe that it is evident that both the petroleum industry and government have accepted the challenge. We in API hope and believe our present program will go far toward improving our own capability for coping with all types of oil spills.

We devoutly hope that this capability, once developed, will not have to be put to use often, but at the same time we recognize that we cannot afford to operate without it.

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Federal Research And Development Program For Oil Spills

Allen Cywin
Director, Division of Applied Science and Technology
Federal Water Pollution Control Administration

Oil which powers our industry, lubricants which keep our wheels turning, and petroleum derivatives which supply so many of our products–are all essential to our national well-being. Unfortunately, mechanical failures, human accidents and negligence, as well as natural disasters, provide all too frequent means for releasing oil and/or its products to the water environment.

The largest source of oil pollution is directly attributable to incidents connected with transport–by river and lake barges, by tank ship, by pipelines, and by road and rail tank cars. The prodigious volumes of crude and refined products transported by sea alone, is illustrated by the fact that petroleum cargo substantially *exceeds the combined tonnage* of all other commodities.

And of course, the potential for oil pollution is not limited to the seas or to transportation. The operations and practices of drilling, production, refineries, petrochemical plants, storage facilities and industrial operations all can contribute to oil pollution of sub-surface, surface, river and marine waters.

Fortunately, both industry and Government have recognized the problem associated with the oil activities, which are so critical to our present way of life, as is evidenced by this jointly sponsored conference!

Government and industry are working together in responding to these unfortunate spill incidents and in many instances are exercising great ingenuity to quickly and easily cope with the problem. But, in many more instances, we have had to resort to slow, costly, backbreaking labor to repair the damage we were unable to prevent. I think everyone here who has been involved in an oil spill incident recognizes the need for a concerted effort to develop new devices and techniques to ideally prevent–but when and if this is not possible–to control and minimize damage to water uses.

A number of public and private agencies have conducted useful work on various subjects related to oil pollution control for the past 10 years or more. However, this was aimed at preventing relatively small discharges from watercraft and industrial operations and improving ship safety.

Helpful as these developments may have been, we were almost totally unprepared to cope with the recent succession of spill incidents that have occurred with far from monotonous frequency. These discharges of oil have come not only from tankers and offshore oil rig but also from storm sewers.

In May 1967, the President of the United States directed the Secretaries of the Interior and Transportation to examine how the resources of the Nation could be mobilized against pollution from this source.

A basic conclusion of the subsequent report to the President, in February 1968, was that adequate means do not now exist to protect this country from large accidents from the effects of pollution caused by oil and hazardous materials.

Recommendations contained in the report have been used as a basis for action by several Government agencies to at least improve our capability in this regard. These recommendations fall into five categories:

1. Additional legal authority.
2. Development and strict enforcement of anti-pollution regulations.
3. The strengthening of international conventions and treaties.

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4. An expanded program of research and development.
5. Additional funding.

The remainder of my remarks will be directed primarily at category four, research and development activities, and more specifically, the Federal Government's research and development effort. But, just as any good R&D program cannot be separated completely from the realities of field operations, enforcement and funding, it will be necessary that I touch on these matters as I go along.

The Federal program of research, development, and demonstration in the field of oil and hazardous substance spills is just emerging from the planning stage and beginning to make progress.

The coordination of Federal oil pollution control R&D program is, in fact, carried out under the auspices of a permanent task group of the National Interagency Committee for Control of Pollution by Oil and Hazardous Materials, a body formed to plan and coordinate the Federal response to future oil spill emergencies. This task group is made up of representatives from the Departments of Defense, Health, Education, and Welfare; Transportation; Interior and the Office of Emergency Preparedness.

The responsibility for conducting needed research, development and demonstration activities has been agreed to among the member agencies in accordance with their capability to undertake these activities, their overall mission as an agency, and their responsibilities within the National Oil and Hazardous Material Pollution Contingency Plan.

The areas of R&D interest and capability of the members are as follows:

Department of Defense

The Department of Defense, through the Navy and the Army Corps of Engineers, consistent with operational requirements, may provide assistance in critical pollution incidents by maintenance of navigation channels, salvage, and the removal of navigation obstructions. Primary areas of research and development activity are the development of devices and techniques to prevent and cope with oil spills from naval vessels and installations.

Critical ballasting requirements imposed by design requirements for warships make it particularly difficult for these vessels to come into port without discharging oily ballast water. Fueling and refitting operations at a number of naval installations have created chronic oil pollution problems. The Navy is accordingly proceeding with R&D programs aimed at: 1. developing practical shipboard systems for preventing oil pollution attributable to discharge of bilge and ballast water from naval ships; and 2. developing equipment and procedures for use by Naval Shore Facilities to prevent, control, and clean up oil spills in harbor waters.

Department of Health, Education & Welfare

The Department of Health, Education, and Welfare is responsible under the terms of the contingency plan for providing expert advice and assistance in incidents that constitute a threat to public health.

Research and development interests include the effect of oil and hazardous materials used in spill cleanup activities on commercially valuable shellfish and in fresh waters, on the use of the water for public water supply purposes. The disposal of solid wastes generated in cleanup operations and air pollution which might be created by attempts to burn oil at the spill site are also of interest. Oil pollution associated with ocean disposal of municipal and industrial solid wastes is being investigated in conjunction with an assessment of current ocean disposal practices.

Office of Emergency Preparedness

The Office of Emergency Preparedness maintains an awareness of pollution incidents as they develop in preparation for coordinating the Federal response if the incident should be a part of a major disaster declared by the President. There is no specific research and development activity in connection with their responsibility.

Department of Transportation

The Department of Transporation, through the U.S. Coast Guard, supplies expertise for the Federal response in the fields of navigation, shipping surveillance, port safety, and maritime law enforcement. Research and development activities are directed at development of aids to navigation, salvage and the development of devices and techniques for use on the high seas for spill detection, containment and cleanup.

Primary R&D emphasis has so far been placed on the development of an air deliverable salvage system to be used to off-load tankers in distress, remote sensing techniques to detect and track oil slicks, and high precision harbor navigation systems and devices to contain spilled oil at sea under adverse sea state conditions.

Department of The Interior

The Department of the Interior, primarily through the Federal Water Pollution Control Administration, is responsible for developing plans to cope with oil spills as well as providing technical expertise relative to water pollution control techniques and the effects of pollutants on aquatic life and other water uses. Consistent with this responsibility, the FWPCA is concentrating its R&D efforts *primarily* in the areas of prevention, containment and cleanup in sheltered and inland waters, the determination of the fate and ecological effects of oil spills in these waters, as well as devices and techniques to clean oil contaminated beaches.

The program is conducted in conjunction with, and receives a spin-off from, a much broader program designed to support the agency responsibility for implementing the Federal Water Pollution Control Act and Water Quality Standards established under the provisions of the Act. This includes the development of advanced waste treatment concepts, industrial pollution control technology, pollution surveillance techniques and techniques to determine the effect of pollutants on water uses.

The Department of the Interior is unique among the members of the NIC in that it has a dual interest in the oil spillage problem. It is responsible for the Federal role in the development of our oil resources as well as the protection and enhancement of the quality of our water resources.

The Bureau of Mines and the Geological Survey while pursuing their respective responsibilities for programs to ensure maximum utilization and prevent waste of petroleum resources, are extremely conscious of the importance of preventing damage or pollution of the environment. Research conducted by both agencies has produced a great deal of knowledge pertinent to the prevention of oil pollution. The Fish and Wildlife Service, Bureau of Land Management, Bureau of Outdoor Recreation, Office of Water Resources Research–in fact almost every major Interior program–has some interest and involvement in preventing oil pollution.

The Department is also unique with regard to its past cooperative programs with industry in finding solutions to many of the other pollution problems associated with the extraction, refining and distribution and industrial use of petroleum.

A brief description of some of the Federally sponsored cooperative projects which are now underway and aimed at solving problems associated with industrial discharges, is included in Table I.

All of the members of the Task Group and a number of other Government agencies, including the Maritime Administration and N.A.S.A., are making significant contributions to the improvement of our defense against oil pollution.

Oil spills must of course be *prevented* to the maximum possible extent. The Coast Guard, in addition to work conducted on navigation aids and other means for preventing maritime accidents, is supporting development of an air transportable salvage system to be used to off-load stricken tankers before the cargo can be lost.

The FWPCA is investigating techniques for gelling tanker cargoes to prevent loss in the event of an accident.

Two separate approaches are being developed: one involves emergency gelling of tanker cargoes; the other, routine transportation in a semi-solid state.

Both the Navy and the Maritime Administration are strongly committed to programs to control pollution from vessel bilge and ballast water discharges. The Maritime Administration program has developed to the point of demonstration of a shipboard system this spring. The system, based on a filter separator design developed by AMF, will reduce oil concentrations in the discharge to 100 mg/l or less.

Work is underway, as indicated earlier, on the control of pollution from a variety of refinery and industrial sources. The largest, in terms of size, is a cooperative program with the American Oil Company to evaluate a 30 MGD unit, employing biological conditioning, chemical coagulation, and air flotation to provide high quality refinery effluent.

Work is also underway under a grant to the National Oil Recovery Corporation in Bayonne, New Jersey to demonstrate an improved oil re-refining process to reduce pollution caused by promiscuous dumping of used oil by local users such as gasoline stations, railroad yards, and machine shops.

Surveillance is needed for basically two purposes–enforcement and operational control of spill cleanup. Airborne remote sensing systems developed originally by the military, show promise of application in the detection of oil slicks at night and under conditions of limited visibility. Considerable effort is being devoted to development of the potential applications of radar, photographic, infrared, ultraviolet and microwave imaging systems. The Santa Barbara incident with its 800 square mile slick provided an excellent opportunity to determine capabilities in the various spectral regions. The most comprehensive study at that site was conducted by the University of Michigan utilizing their multispectrum scanner.

Preliminary information indicates good contrast between oil and water in the ultraviolet, far infrared and microwave regions. Fundamental work on this subject is being carried out by the Coast Guard under contracts with the University of Michigan and Aerojet General. N.A.S.A. has also supported and cooperated with other agencies on a great deal of work on remote sensing techniques, much of which is applicable in the remote sensing of oil slicks.

Instruments to monitor oil concentrations are being developed as a part of a project being carried out for us by the City of Buffalo. Also, a project is being conducted for the Maritime Administration by the Illinois Institute of Technology Research Institute (IITRI). The instrument developed at Buffalo utilizes a series of conductivity probes to permit remote sensing of oil accumulation in sewers. The IITRI instrument employs an infrared absorption technique to monitor oil concentrations in bilge and ballast water.

In addition to the surveillance capability under development, Federal enforcement responsibilities require the development of techniques to positively identify the source of spilled oil. This is needed primarily for small spills caused by bilge and ballast water discharges or fuel transfer accidents where the source is difficult to trace. A variety of analytical techniques may be applicable.

Neutron activation analysis techniques are being developed by Gulf General Atomic for the AEC; however, more must still be learned about the effects of weathering (i.e., evaporation, biological attack, oxidation, etc.) on the inherent characteristics of oils that might be used as identifiers.

The feasibility of adding chemical, radiochemical and particle tags to tanker cargoes is also being investigated, under contract by Melpar, Incorporated.

Behavior of Floating Oil

The fate and behavior of floating oil vitally important information in planning spill cleanup operations, is under study as a part of several projects.

Studies of fundamental factors influencing slick movement are under study as part of projects at MIT and NYU.

TABLE 1. ONGOING GOVERNMENT RESEARCH & DEVELOPMENT PROGRAMS

Project Title/Description	Sponsor	Investigator	Estimated Project Cost	Remarks
Prevention of Oil Resease				
1. In-Tank Gellation to Reduce Oil Loss From Tankers	Federal Water Pollution Control Administration	Western Company Richardson, Texas	$ 230,674	Develop onboard and portable systems to gel oil rapidly in leaking tanker compartments
2. Development of Equipment for Control of Oil Spillage & Systems for Aerial Delivery	U.S. Coast Guard	Ocean Science & Engineering Washington, D.C.	290,760	Air transportable tanker emergency unloading equipment
3. Treatment of Oil Wastes through the use of Emulsion Agents	FWPCA	Sonics International, Inc.—Dallas, Texas	43,056	Determine feasibility of transporting oil in a viscous emulsified state
4. Oil-Water Instrumentation	U.S. Maritime Administration	Illinois Institute of Technology	180,000	Development of a device to monitor oil concentration in ballast and bilge waters
5. Shipboard Oil-Pollution Control Systems for Ballast & Bilge Waters	U.S. Navy	U.S. Navy Washington, D.C.	—	Development of systems to prevent oil pollution attributable to bilge & ballast water from naval ships
6. Demonstration of the Complete Conversion of Crankcase Waste Oil Into Useful Products Without Producing Pollutant Material	FWPCA	National Oil Recovery Corp. Bayonne, New Jersey	1,530,000	Demonstrate improved rerefining process which will stimulate reuse of used lubricating oil
7. Oil-Water Separation	U.S. Maritime Administration	AMF Cuno Stamford, Conn.	180,000	Development & demonstration of a high capacity oil-water separator for bilge & ballast waters
8. Evaluation of Polymeric Materials for the Treatment & Recovery of Petro-chemical Wastes	FWPCA	Dept. of Commerce & Industry State of Louisiana	68,992	Evaluation of reverse osmosis membranes for application to in-plant chemical waste
9. Preliminary Investigation Requirements-Petrochemical & Refinery Waste Treatment Facilities	FWPCA	Engineering Science Inc. Arcadia, California	17,000	Preliminary waste water treatability study
10. Treatment of Waste Water-Waste Oil Mixtures	FWPCA	Armco Steel Corp. Middletown, Ohio	1,541,000	Construction & evaluation of chemical treatment plant for oil-water emulsion from cold rolling mill
11. Metal Ion-Catalyzed Oxidation of Phenols & Aromatic Amines	FWPCA	Texas A&M Research Foundation	234,000	Evaluation of treatment process
12. State-of-the-Art Evaluation of Petroleum & Coal Wastes	FWPCA	University of Oklahoma Research Institute Norman, Oklahoma	17,897	Report on present practice with recommendations for future research
13. Efficiency of Fibrous Bed Coalescers	FWPCA	Illinois Institute of Technology—Chicago, Ill.	65,000	Development of a mathematical description of the process
14. Fluid-Bed Incineration of Petroleum Refinery Waste	FWPCA	American Oil Company Chicago, Ill.	354,530	Construction and evaluation of fluid-bed incineration system

TABLE 1 (Continued)

Project Title/Description	Sponsor	Investigator	Estimated Project Cost	Remarks
15. Improved Capabilities of Biological Systems to Assimilate Oil	FWPCA	American Petroleum Institute New York, N.Y.	84,990	Laboratory study of effect of hydrocarbons on activated sludge water treatment system
16. Treatment of Refinery Effluent by a Unique Combination of Biological & Chemical Processes	FWPCA	American Oil Co. Chicago, Ill.	1,737,795	Demonstration of 30 MGD chemical coagulation air flotation & biological conditioning
17. Oil Dispersion Coalescence by Porous Solid Contact	FWPCA	Harvard University Cambridge, Mass.	16,157	Determination of fundamental factors influencing performance
Surveillance				
1. Multi-Spectrum Scanning to Determine Oil Slick Fate	FWPCA/Geological Survey	University of Michigan Ann Arbor, Michigan	31,000	Determination of multispectral radiation characteristics of crude oil in the Santa Barbara Channel, February 1969
2. Investigation of Ultraviolet & Infrared Spectra of Oil Slicks	U.S. Coast Guard	University of Michigan Ann Arbor, Michigan	52,694	
3. Investigation of Microwave Measurements of Oil Slicks	U.S. Coast Guard	Aerojet General Corp. El Monte, Calif.	48,285	
4. Microwave Radiometric Measurement of Oil & Sea Temperature	National Science Foundation—Office of Sea Grant Programs	University of Calif. Santa Barbara	38,000	Static Tests
5. The Spreading of Oil Films	FWPCA	New York University Bronx, New York	27,000	Laboratory investigation of fundamental factors influencing oil slick movement
6. Chemical Determination of Source Pollutant Tars	National Science Foundation—Office of Sea Grant Programs	University of Calif. Santa Barbara	16,500	Heavy metal concentrations in natural seeps & production crude oil
7. Investigations of Surface Films—Chesapeake Bay Entrance	FWPCA	Virginia Institute of Marine Science Gloucester Point, Va.	57,652	Determination of effect of wind, wave & current regimes of oil films
8. Oil Tagging Systems Study	FWPCA	Melpar Inc. Falls Church, Virginia	50,000	Determine operational systems for tagging petroleum & petroleum products with chemicals & other identifying tags
9. Oil Slick Source Identification	Atomic Energy Commission	Gulf General Atomic San Diego, California	73,000	Neutron activation analysis to determine characteristic trace metals
10. Oil Spill Analysis	National Bureau of Standards	National Bureau of Standards	20,000	
11. Detection, Identification & Determination of Oils, Tars & Slimes by Reflectance Spectroscopy	FWPCA	University of Michigan Ann Arbor, Michigan	36,779	Application of the technique to analytical methods and continuous monitoring

TABLE 1 (Continued)

Project Title/Description	Sponsor	Investigator	Estimated Project Cost	Remarks
Control				
1. Prevention & Elimination of Oil Pollution in the Buffalo River	FWPCA	City of Buffalo Buffalo, New York	$ 737,194	Cornell Aeronautical Laboratory subcontractor develop & demonstrate equipment and techniques to detect, sample, contain & collect oil entering the Buffalo River
2. Test & Evaluate Mechanical & Pneumatic Barriers to Contain Spilled Oil & Means for Removing the Contained Oil in Harbor & Adjacent Waters	FWPCA	Maine Port Authority Portland, Maine	100,850	Determine effectiveness & develop techniques for utilization of available containment & recovery systems
3. Analysis of Methods for Removal of Oil from Harbor Waters	U.S. Navy	Battelle-Northwest Richland, Washington	16,750	Cost effectiveness study of available equipment
4. Collection of Spilled Oil With the Aid of Foams	FWPCA	City of Cleveland Cleveland, Ohio	98,300	Horizons, Inc., sub-contractor oil recovery system
5. Oil-Water Separation System for Treatment of Oil Wastes	FWPCA	Garrett Corp. Los Angeles, Calif.	78,178	Oil harvesting device & high capacity (500 gpm) centrifuge
6. Investigation of Recovery of Large Marine Oil Spills by Use of a Vortex Assisted Air Lift System	FWPCA	Battelle-Northwest Richland, Washington	29,880	Pilot scale demonstration
7. Evaluate Stresses on High Seas Oil Booms	U.S. Coast Guard	Hydronautics Inc. Laurel, Maryland	62,790	Model Basin studies
8. Evaluate Use of Sand for Sinking of Oil Slicks	U.S. Coast Guard	U.S. Army Corps of Engineers	10,000	Determine feasibility of utilizing existing hopper dredges to disperse sinking agent.
9. Containment & Collection of Oil in Protected Waters	FWPCA	Massachusetts Institute of Technology Cambridge, Mass.	150,000	Seven individual studies directed toward development of design data containment & harvesting systems
10. Molecular Interactions at the Oil Water Interface & formation of microemulsions	FWPCA	Columbia University New York, New York	30,257	Study of factors influencing effectiveness of dispersants
11. Effectiveness Criteria for Dispersants	FWPCA	FWPCA Edison, New Jersey	–	Criteria for evaluating effectiveness of oil dispersants
12. Microbiological Seeding of Accelerate Degradation of Hydrocarbons	FWPCA	Florida State University Tallahassee, Florida	118,460	Techniques including seeding with selected cultures, nutrients & other additives will be developed
13. Bio-degradation of Oil Slicks	U.S. Navy	Rutgers University New Brunswick, New Jersey		Determination of factors influencing oil biodegradation
14. Collection of Floating Oil in Harbors	U.S. Navy	U.S. Navy Port Hueneme, Calif.		Study of equipment & methods
Effects				
1. Treatment of Waterfowl Trapped in Oil Polluted Waters	FWPCA	University of Calif. San Diego, Calif.	31,000	Determine factors contributing to death, develop methods of cleaning and managing birds in captivity

TABLE 1 (Continued)

Project Title/Description	Sponsor	Investigator	Estimated Project Cost	Remarks
2. Abundance & Composition of Deep & Shallow Water Macroplankton & Littoral Fish Population in and about Santa Barbara Channel	FWPCA	University of Calif. Santa Barbara	17,300	Determination of the effects of the February 1969 oil spill
3. Preliminary Study of Oil Spill Damage in the Intertidal Regions of Santa Barbara & Ventura Counties, California	FWPCA	University of Calif. Santa Barbara	7,200	Determination of the effects of the February 1969 oil spill
4. Fishes of the Santa Barbara Kelp Forest	National Science Foundation—Office of Sea Grant Programs	University of Calif. Santa Barbara	18,000	Ecological Study
5. Population Dynamics of Inter-tidal Organisms	National Science Foundation—Office of Sea Grant Programs	University of Calif. Santa Barbara	29,000	
6. The Effects & Implications of Petroleum Pollutants on Resources of the Santa Barbara Channel	National Science Foundation—Office of Sea Grant Programs	University of Calif. Santa Barbara	13,000	
7. Interaction Between Marine Organisms & Oil Pollution	FWPCA	Woods Hole Oceanographic Institute, Woods Hole, Mass.	150,000	Determination of the chronic & sublethal effects of hydrocarbons on marine organisms
8. Relative Toxicity Test for Dispersants & Oil Dispersant Mixtures	FWPCA	FWPCA-West Kingston, R.I.	—	Development of standard methods for determining toxicity to aquatic organisms
Beach and Shore Restoration				
1. Feasibility Analysis of Incinerator Systems for Restoration of Oil-Contaminated Beaches	FWPCA	Aerojet General Corp. El Monte, California	35,551	Evaluation of alternative combustion systems for removing oil from sand
2. Application of Froth Flotation Separation to Beach Restoration	FWPCA	Melpar Incorporated Falls Church, Virginia	304,168	Demonstration of 30 Ton/Hr capacity plant
3. Evaluation of Selected Earth Moving Equipment in Beach Restoration Operations	FWPCA	URS Systems Corp. Burlingame, California	172,489	Evaluate selected earth moving equipment, make appropriate minor modifications and develop and demonstrate operating procedures
Other				
1. Identification of R&D Requirements	U.S. Coast Guard	A.D. Little Cambridge, Mass.	47,235	
2. Documentation of Cleanup Experience Following the Oil Spill Disaster at Santa Barbara, California	FWPCA U.S. Coast Guard	Battelle Memorial Inst. Richland, Washington	24,000	Document causes and affects and effectiveness of measures tried to contain and clean up spilled oil

The effects of oil pollution and various potential cleanup techniques on marine life are under study. Santa Barbara again is serving as a good laboratory. A number of diverse studies by biologists at the University of California, Santa Barbara, and the University of California, San Diego, to determine the effect of the spill on marine life are close to completion. Fortunately, a sizable amount of baseline data exists on pre-spill conditions so that a good comparison should be possible. We are, incidentally, supporting a project to improve the plight of birds unlucky enough to get involved in a spill. The study of techniques to clean and rehabilitate oiled birds is underway at the University of California, San Diego.

Less spectacular, but as important perhaps in the long run, is a study recently initiated at Woods Hole to determine the subtle long term effects of hydrocarbons on marine life.

But knowledge of where the oil is going and what it is going to do is of questionable value if we do not have the capability to *control* it. By far, the greatest effort at the Federal Government level is being expended to develop devices and techniques to contain and recover spilled oil.

Devices which are presently commercially available for containment and oil recovery are being evaluated and demonstrated at the Buffalo, N.Y., and Portland, Me. Both are FWPCA sponsored projects. Although many of these devices have a valid place in our arsenal of cleanup tools, we are at the same time striving to develop recovery equipment which will have an order of magnitude of greater recovery capacity under much more severe environmental conditions. Barrier devices, which will combine economy and ease of deployment with the all important requirement of adequate structural strength and effectiveness under the severe wind, wave and current conditions that might be expected to accompany a marine disaster, are also being developed.

A major effort thus far has been devoted to determining the fundamental factors influencing barrier effectiveness and strength. While many barriers have been fabricated commercially, a somewhat smaller number have retained their structural identity in use, and a smaller number still have performed satisfactorily. A major effort in the area of barrier development is thus planned for this fiscal year.

The Coast Guard is carrying the major portion of the burden in this regard. A study of factors influencing boom performance at sea was conducted by Hydronautics, Inc., for the Coast Guard. This data was used as the basis for a request for proposals several months ago.

Mechanical Recovery and Separation

Several concepts for mechanical recovery and separation of the oil-water mixture recovered are also under development. The basic objective is, of course, to collect floating oil at a high rate under adverse wind, wave and current conditions, while minimizing the amount of water collected. Both high efficiency oil pickup unit processes and high efficiency oil-water separator units will be required. Several novel applications of centrifugal separation are under development. FWPCA is negotiating on proposals submitted in response to a recent RFP on recovery of spilled oil. The proposed concepts are very intriguing and show real promise of vastly improving the state of the oil recovery art.

In addition, work is underway which we hope will give us a better insight into the use of sorbents, dispersants and burning agents for use in oil spill cleanup operations. In view of the great number of agents being proposed, we see the Government role in this regard as more of an advisor than the developer of techniques. Industry is much better able to efficiently develop this area than we are. We are limiting our efforts to the development of tests and standards for equitably evaluating the various products.

Performance tests and techniques developed in FWPCA laboratories to evaluate dispersant effectiveness and toxicity will be discussed in detail with representatives of industry later this week. Agreement on procedures we all can use to evaluate the enormous array of both commercially available and potentially useful materials would be most beneficial.

The interesting idea of accelerating the natural biological degradation of oil slicks is also being studied. Dr. Oppenheimer of Florida State University will report on this work on Wednesday.

Although both industry and Government are striving to improve our capability to prevent as well as clean up oil slicks before they reach shore, there is not much doubt that we will still need improved techniques and devices to clean up beaches and shore features contaminated by spills that get out of hand or are discharged clandestinely.

Thus, several projects are underway to improve the capability of physically removing oil from beaches without inadvertently taking large quantities of clean sand.

Modifications to common earthmoving equipment and operating procedures are being developed and will be demonstrated this spring by FWPCA. The feasibility of sand cleaning processes involving incineration, are also being determined.

A full scale, 30 ton per hour froth flotation beach cleaning plant is under development and will be demonstrated this summer.

To summarize this overall Federal research, development, and demonstration program, I think it is fair to say that we are now beginning to look in the right places for the answers to the most significant problems.

We have endured our *Torrey Canyons, Ocean Eagles,* and "Santa Barbaras" and are beginning to develop a capability to react in a much more efficient manner to these incidents. But, we need to do much more. By *we*, I refer to both Government and Industry. The problem is too large and our present body of technology too small to waste time and money in talking about the problem or in duplicating the work of others. We hope that the Federal Government can work closely with industry to make certain that every dollar and every day counts—in the true spirit of our great American system!

United Kingdom Oil Industry Research And Plans To Deal With Sea Pollution By Oil

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Abstract

The Institute of Petroleum has consistently provided for the exchange of knowledge and opinions on technical matters of a non-commercial nature relating to the oil industry. It has also provided a link between Government departments and the U.K. oil industry on a wide variety of technical matters ranging from measurement, sampling and testing to the conditions of license for the storage of petroleum spirit (gasoline). It is not surprising therefore that the Institute is the focal point of coordination between U.K. oil companies on the prevention of pollution by oil and provides a link between these oil companies, interested Government departments, the tanker industry and a number of international organizations. This paper traces the development of the Institute's role in the field of prevention of oil pollution and reviews the present position of cooperative research and response plans.

Early U.K. Anti-Pollution Activities

Individual oil companies in the U.K. had been concerned for some time with the effects of oil spills on local amenitites when the first phase of refinery expansion got under way in the immediate post war years. The new refinery constructions in Europe in the late 1950's resulted in increased awareness of and concern over the risks of oil pollution and the Institute had a paper presented in 1962[1] on the subject of "Oil Recovery and Removal". At the same time the Warren Spring Laboratory at Stevenage, now part of the Ministry of Technology, was concerned with the development of methods for the removal of oil from beaches so that it could provide advice through the Ministry of Housing & Local Government to the local authorities which in turn were involved in beach cleaning in their respective coastal areas.

By the mid-1960's, increased oil tanker traffic to U.K. refining centers and around the British Isles to other European countries, together with increases in general shipping in oil burning vessels, gave rise to increasing public alarm at the frequency of coastal oil pollution incidents. The U.K. Advisory Committee on the Prevention of Pollution of the Sea by Oil—was set up in 1952 under the Chairmanship of the Rt. Hon. James Callaghan—now Home Secretary in H.M. Government—by representatives from all the major U.K. conservationists bodies, the hotel and catering industry, travel associations and local government.

By having official observers at its meetings the major oil companies were informed of the growing concern and pledged to give all possible assistance. It was in these circumstances that "Load on Top" was developed to minimize the quantity of oil discharged to sea following the tank washing operations which are a necessary part of the routine followed by tankers on the return journey to the crude oil loading ports. Seven oil companies declared their immediate adoption of "Load on Top" for their own tanker fleets and time charter vessels and to publicize the procedure and to secure its wider adoption, they produced a twenty minute instructional film on the subject in conjunction with the U.K. Advisory Committee.

Beach Pollution by Oil

Meantime the Institute was concerning itself again with the problem of beach pollution and beach cleaning and in 1966 set up, in conjunction with the Ministry of Housing & Local Government, a Committee to establish the true extent of the problem and to recommend a suitable organization and methods to deal with it. This committee had its report in final draft form when *Torrey Canyon* ran aground in March, 1967, and although the final report was not submitted to the Ministry until June, 1967, there were no significant amendments to the report as a result of *Torrey Canyon* experience. The report recommended the appointment by county authorities around the coast of England, Wales and Scotland of pollution officers responsible for coordinating the beach cleaning plans of the county and of the subordinate rural and urban authorities in the county. It suggested that the these plans should include the training of personnel, the holding of some specialized stocks such as oil dispersant chemicals but especially that the plans should include the collation of information on the availability of spraying equipment, mechanical equipment and of boats suitable for treating oil slicks up to one mile from shore.

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[1] Superior numbers refer to literature references at conclusion of text.

The report also listed the latest information available to the oil industry and to Warren Spring Laboratory (which was represented on the Committee) on oil clean-up procedures. By July 1968 the Minister had agreed to accept the recommendation of the report in full and issued a circular to all coastal county and county borough authorities in England asking that oil pollution officers be appointed and that emergency clean up plans be prepared. Corresponding instructions were also issued in Wales and Scotland. Central Government bears half the cost of approved oil clean-up operations carried out by the local government bodies. In both the I.P. report and the Government circular to county authorities, the recommendations are concerned with oil on beaches and up to one mile out to sea.

Torrey Canyon and After

When *Torrey Canyon* ran aground the major U.K. oil companies set up a Technical Committee to ensure that industry knowledge was available to the Government forces engaged in tackling the oil spill. This committee was soon 'adopted' by the Ministry of Power and made official by the appointment of Sir Charles Cawley, its Chief Scientist as Chairman. Central Government also set up a committee of scientists under Sir Solly Zuckerman, the Chief Scientific Adviser to the Government. The Cawley Committee presented a report[2] to the Minister of Power in the Fall of 1967 and most of its recommendations were contained in the Zuckerman Committee report[3] that was issued at the year end.

Concern over the delay between the *Torrey Canyon* incident and the publication of any Government recommendations resulted in the Institute of Petroleum setting up its Coordinating Committee on the Prevention of Sea Pollution in December, 1967. Its terms of reference are "To consider, encourage and coordinate worthwhile contributions by the oil industry in dealing with the effects of oil pollution at sea and in tidal waters". The two Government committees had been concerned with matters of a marine nature as represented by the Chamber of Shipping in addition to those involving petroleum technology represented by the Institute of Petroleum. It was agreed in discussions with the Chamber of Shipping that the Institute's Coordinating Committee would consider primarily the contributions of the land based oil industry establishments and provide liaison with the marine interests through Chamber of Shipping members from oil company marine departments who were on the Cawley Committee and became members of the Institute's Coordinating Committee. The Committee also extended invitations to representatives from three Government departments directly concerned with sea pollution prevention and subsequently to a member of CONCAWE's staff to join its ranks.

The Coordinating Committee has four working groups dealing respectively with:

1. The behavior of oil at sea and on foreshores
2. Burning of oil
3. Detergents and their application
4. Sinking, absorbing and coagulating materials

Behavior of Oil at Sea

Progress on the studies of behavior of oil at sea were reviewed in a Symposium at the Institute in London on October 2nd, 1968, the proceeds of which were fully documented in the I.P. Review of November, 1968. The rate of movement of an oil slick in relation to existing wind and tide conditions can be predicted fairly accurately.

Weathering will take place quite rapidly in the case of crude oil but a number of unknown factors may influence the ultimate spread of the oil resulting, in some cases, in films of mono-molecular proportions and in others in the formation of water in oil emulsions many inches thick. The Ministry of Defence has now appointed a research coordinating group to carry out studies into the behavior of oil at sea and has invited the I.P. Working Group members to combine in this wider activity, providing basic know-how and making recommendations for areas to be further investigated.

Burning of Oil

The group on burning oil has concerned itself with the possibilities of burning oil in stranded vessels, on the sea and on beaches. It has been joined by Government Laboratory personnel working in this field and it is at Government establishments that most of this work is now being done. Tests using tanks of about 3 square feet cross section have established burning rates, with varying apertures in the roof and in the side of the tank.

Detergents and their Application

There is little doubt that the solvent/emulsifier materials widely used for beach cleaning and for dispersing oil at sea—and especially in cleaning up after *Torrey Canyon*—cause more damage to marine flora and fauna in the inter-tidal area than would be caused by the oil itself. The light aromatic solvent appears to be the most toxic component and excessive use of solvent/emulsifiers in relation to the quantity of oil to be removed is clearly an important factor. This group was therefore charged with the assessment of the effectiveness of the various available detergents in relation to their cost, toxicity and the best methods of application.

A separate paper on the evaluation of oil dispersing chemicals is to be presented by Ray Beynon, the Chairman of this particular group, and other papers deal with toxicity problems. I will leave the discussion of this work to others. It is perhaps worth mentioning here that as a result of the general awareness of the need for less toxic oil dispersant chemicals, following *Torrey Canyon* experience, no less than three such materials have been produced as a result of work in commercial laboratories—one in the U.S. and two in the U.K.

Sinking, Absorbing and Coagulating Materials

This group is concerned with methods of treating oil spills other than by burning or by chemical dispersion and with recommending preferred methods for given situations.

Tests on the laboratory scale have suggested that a variety of materials have potential for sinking oil, but problems of application arise when full scale application is considered. Most of the larger scale tests have been carried out by the Ministry of Technology in conjunction with the Ministry of Agriculture and Fisheries and will be described in detail by authors from these departments. To overcome the logistic problems associated with using say a manufactured chemical from a source remote from an oil spill, one oil company has considered the use of sand dredged from the nearest sand bank to an oil spill and treated on the dredger before application. Full scale tests to establish the sinking effectiveness and the quality of any residual oil slick are being contemplated.

To date, we have no reason to share the confidence displayed by the French authorities in the effectiveness of sinking procedures and our fisheries people are concerned as to the effects of sunken oil on fishing gear.

Absorbing materials have long been used for removing oil from effluents in such devices as hay filters. Straw is an excellent material for collecting heavy oil as it comes ashore but requires large manpower resources. Attempts to improve on these materials have resulted in the use of synthetic materials with oleophylic and hydrophobic qualities.

Polypropylene and polyurethane have been tested extensively and the latter has been used successfully in cleaning up actual spills in restricted waters. In U.K. applications the polyurethane has been shredded to give crumbs of ½ inch to 1 inch size. Difficulties arise in collecting the oily material after absorption of oil has taken place. Israeli claims suggest that a blanket structure—possibly a loosely scintered arrangement of the shredded material—has been used effectively in crude oil clean-up work following damage to crude oil pipelines.

Polyurethane has been used also as the oil absorbing surface on cylinders mounted in front of vessels to collect oil from polluted water. Work has been done also on series of parallel discs to pick oil from water surfaces since these provide more collecting surfaces than on a cylinder of similar overall length and on endless belts of absorbent material. All these devices have value in calm sheltered waters but have very limited rates of oil recovery.

A variety of methods have been used for skimming and sucking oil off the sea. Some include provision for booms in V formation ahead of the craft to concentrate the oil at suitable inlet nozzles. All have severe limitations as to the wave height in which they can operate and in the quantity of oil they handle and separate. There is, as yet, no oil recovery equipment suitable for effective use in a major oil spill incident.

Floating booms of varying design are commonly used to contain oil spills, especially fuel oil spills, where removal rather than dispersion is contemplated. While their effectiveness is restricted to sheltered w[illegible] little wave or tidal movement, they are useful in selected incidents. Manufacturers have produced a variety of new booms and an evaluation of these is being undertaken by the Government Hydraulics Laboratory.

Sponsored Research

In addition to these various investigations into improved methods of treating oil spills, the Institute has an interest in the overall effects on marine flora and fauna. A three year research grant has therefore been made jointly with the World Wildlife Fund to the Field Studies Council to support work by two graduates into the biological and zoological effects of oil pollution at the inter-tidal zone. This work has been in progress for two years and the second annual report contains some very significant indications. Environmental damage from accidental crude oil spills is stated to be slight in most cases "provided detergent/emulsifier compounds are not used". There are indications that winter oil spills, say from January to April, are more serious than those involving the same materials in late spring, summer or fall. In some cases growth promoting effects are reported. On the other hand, continuously occurring pollution by oil effluent water allows little opportunity for recovery and cumulative damage may be significant.

Yet another area of research in which the Institute has provided help is into the recovery and rehabilitation of oiled seabirds. In 1967 the bird preservationists of the U.K. Advisory Committee on Oil Pollution asked for help in setting up a seabird research unit. The Institute suggested that a literature survey be carried out before making any major commitment and provided financial assistance for this to be done. The report "Rehabilitation of Oiled Seabirds" by Professor L.B. Clark and J.R. Kennedy of Newcastle-on-Tyne University was published late in 1968, and has since been used as a basis for a detailed research proposal. As a result of discussions on this proposal at the Institute, six oil companies have agreed to finance a five year research program at Newcastle. Work will commence early in 1970.

U.K. Response Plans

Local Plans. Individual oil companies for a long time have recognized the need to act responsibly in areas where their major activities are located. They have had oil retaining booms, launches and other equipment available at refineries and have developed and manufactured solvent/emulsifiers for treating accidental spills. More recently, the development of Milford Haven as an oil refining center resulted in the companies involved, presently four in number, and the local port authority, forming a cooperative plan to deal with all oil spills in the vicinity.

A specially equipped launch is ready at all times to proceed to an incident and for small unattributed slicks the cost of cleaning is borne by all participants. Where an oil spill can be attributed to one company's operations, that company is responsible for all costs and assumes control of the clean up operations—including the control of the authority vessel. There is provision for the launches and the facilities of all member companies to be made available on a mutual assistance plan basis.

Whether there are major oil company activities in the vicinity or not, many coastal authorities and particularly those with significant tourist business, have also had arrangements under which employees normally on street cleaning or other work could be diverted with suitable equipment to beach cleaning when local pollution was encountered. The combined experience of these various local authorities beach cleaning activities and of the oil companies and cooperative groups in tackling spills in harbours or on local coastlines, were the basis in 1967 of the recommendations to central Government which resulted in a national plan for coastal pollution.

National Arrangements. Following the recommendations submitted to the Ministry of Housing and Local Government by the Institute in September, 1967, the circular of 8th July, 1968, requested all coastal county councils to make the necessary arrangements to clean up oil pollution of beaches and to treat oil slicks up to one mile from shores. Provision was made for the notification of any approaching oil slick by coastguards and by ships or aircraft to local police and thence to county authorities who in turn would relay the information to subordinate authorities. Arrangements have been made in most areas for mutual assistance between adjacent county councils.

As a result of the signing in March, 1969, by Britain and eight other countries of the North Sea Pact, the Board of Trade has been charged with the responsibility of dealing with oil on the seas in excess of one mile from U.K. coasts. The precise procedures to be adopted by the Board of Trade have not been decided at the time of writing. Nine principal officers of the Board of Trade share responsibility for regions of Britain and these are being consulted on available methods of meeting this new requirement. It seems probable, however, that where suitable naval or other Service resources are available these will be used. When these resources are not available, privately owned vessels may be retained and equipped to meet Government requirements.

Thus on receipt of information that an oil slick has been located in a particular Board of Trade area, beyond one mile from the shore, and is likely to cause pollution of beaches or other amenity areas in the U.K. or one of the signatory countries if left untreated, the appropriate Board of Trade office will take action. If the treatment at sea is not effective in preventing oil reaching the one-mile limit, local authority resources will be employed to spray coastal waters and to clear beaches as required.

By the combination of the available resources in several local authorities within a county, and if need be in adjacent countries, a large force of men, equipment and materials can be made available to deal with larger oil contaminations. These combined resources would be insufficient to deal with another *Torrey Canyon* in which most of the cargo was carried into coastal waters. They would, however, form a most valuable nucleus on which to build a major attack, employing army and other emergency forces.

Industry Plans. Events of the past few years have provided grim evidence that large scale pollution by oil can occur anywhere in the world. Oil companies realize that they must be ready at all times to deal effectively with spills which might be attributed to their operations, and have made plans for mobilizing their resources to do this.

To minimize the risk of serious pollution following any collision or stranding of tankers, much greater emphasis has been placed on the salvage of cargo in addition to the hull salvage. A significant factor in salvaging oil cargoes could be the availability in European waters of a number of handy sized tankers, specially equipped to receive cargo from larger crude carriers. These vessels are specially equipped with fendering to facilitate berthing alongside another tanker, and are regularly carrying out the lightening operations at sea to enable the large tankers then to proceed to existing marine terminals. These vessels also carry, as do a large proportion of normal service tankers, oil dispersant chemicals, thus permitting early application in the event of any oil spill incidents.

The recognition of a pollution risk outside major operating terminals necessitates the preparation of plans for dealing with such spills. In a typical example, one company has established a headquarters control center and has designated personnel to man this center and also to man the local field control center to be established whenever an incident occurs. Through liaison with central Government and other national headquarters, information on the names, telephone numbers and locations of all local Government pollution officers, Board of Trade representatives, Fisheries Officers and Local Conservationist Organizations have been card indexed so as to be readily available when any incident occurs.

In the absence of any satisfactory means of physically collecting oil from the sea, reliance is placed on chemical dispersion. Even when essentially non-toxic dispersant chemicals are used, local conservation authorities are required to agree to such usage before application. It is essential, therefore, that rapid contact can be established with these organizations.

In addition to the dispersant normally carried on sea-going tankers, refineries and marketing terminal installations maintain stocks of chemicals and of spraying equipment and in many instances retaining booms and absorbent materials. In addition, limited oil company manpower is available at such installation and designated contractors are available to provide manual labour, mechanical equipment and vessels ranging from small fishing vessels to larger sea-going craft.

Some exchange of information between major companies has already resulted in a widespread knowledge of the availability of men, materials and other resources available to the Industry as a whole. This inter-company information is likely to be placed on a more formal basis in the near future, as is also information on the resources available to local authority organizations and consideration is being made to the formation of regional organizations in which the combined resources of Government, local authorities and oil companies would be available for dealing with any incident.

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United Kingdom Ministry Of Technology Work On Oil Pollution

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Abstract

The work of the various research laboratories of the Ministry of Technology in the field of oil pollution is described. It includes the removal of oil from beaches and from the sea, the burning of oil in tanks and the use of booms in sheltered waters.

In 1960, there were a number of fairly large-scale oil pollution incidents off the south coast of England. As a result, an approach was made to the Minister for Science to carry out work to find out the best method of removing oil pollution from beaches. This work, which was soon extended to the problem of dealing with oil while still on the sea, was carried out by the Warren Spring Laboratory, now part of the Ministry of Technology. Other Ministry laboratories were later drawn in for other aspects of the problem. The work is still going on.

This paper will describe firstly the treatment of oil on the beaches; secondly, methods of dealing with oil on the sea; thirdly, the burning of oil in tanks; fourthly, the use of booms to protect particular sites; and, lastly, other means of preventing oil from reaching the surface of the sea.

Oil Pollution of Beaches

To determine the priorities which should be adopted, a survey was carried out in 1960 among coastal Local Authorities to find out their experience of oil pollution. The least serious, but the most common type of pollution, was found to be the almost continuous arrival of solid, or semi-solid, lumps of oil (commonly called tar) on the western coasts of the British Isles. The next most common type of pollution was from larger quantities of very viscous oil causing heavy contamination of a relatively short section of beach. The third type of pollution, fortunately the least common, was the arrival of much larger quantities of liquid, or semi-liquid, oil. In the last case, it was generally possible to identify the source of the pollution with some particular incident.

A number of alternative methods of dealing with the oil on the beach were proposed, viz:

1. burning;
2. leaving the deposits *in situ* and rendering them innocuous by coating them with various materials;
3. removing mechanically or, by hand; and
4. emulsifying the oil and then dispersing the emulsion by the action of the tide and waves, or by hosing down with water.

Each of these proposals will now be discussed separately.

Burning

At first sight, it would appear that the surest and most effective method for the complete removal of oil is to destroy it by burning. A short laboratory investigation was therefore undertaken to examine the practicability of burning as a technique for the removal of oil deposits and if possible to find combustion promotors which were cheap, effective and easy to apply. Experiments were carried out on a sample of the deposit which was actually collected from a beach, consisting mainly of viscous tarry material containing sand and some liquid oil. Samples of the deposit to be treated were weighed out into silica dishes and heat was applied with a gas/air blow lamp. It was thought that the addition of solid oxidants, such as sodium nitrate and sodium chlorate, would if they were mixed with the oil, promote ignition and aid combustion, by supplying additional oxygen. The oxidant in various proportions up to 30 per cent by weight were sprinkled over the surface of the deposit which was then left for two hours before ignition; in each case a medium flame was applied to the sample under test. Burning soon ceased and attempts at re-ignition under the same conditions failed. As the weight of the oxidant was increased, so the weight of the residue decreased, but in all the tests the residue was of a sticky pitch-like nature.

To obtain a slower burning rate and a better distribution of the oxidant, a combustible carrier in the form of sawdust was employed. The treated sawdust, containing 70 per cent by weight of the oxidant, was then sprinkled over the oil and ignited after standing as before. It was apparent that even in the presence of solid oxidants, incomplete combustion of the oil in the semi-solid tarry deposit was obtained. It was thought that this was probably due to the limited access of air which was sufficient only for the combustion of the lighter constituents of the oil. It was, therefore, considered that the provision of some kind of wick would enable the liquified deposit to be drawn into an excess of air and be completely burned.

Mixtures containing different proportions of solid oxidant and a material such as Kieselguhr or woolly asbestos, which would function as a wick, were sprinkled over the deposit contained in a silica dish and left for one hour before igniting with a gas/air burner. The experiments were repeated under rather more realistic conditions in which the oil deposits were spread over beach pebbles contained in a tray; the oxidant/wick mixtures were added and the material ignited as before. It was observed in this case that the oil flowed to the underside of the pebbles where it was impossible for it to be ignited. The conclusions reached from this set of experiments were as follows:

1. The type of heavy oil normally contaminating beaches and the foreshore is very difficult to burn by ordinary means and combustion ceases when the source of heat is removed.
2. The addition of solid oxidants aids the combustion of part of the deposit, but a sticky, tarry residue is left with medium heat and a residue of dry, black carbon with prolonged intense heat. About 30 per cent by weight of oxidant has to be employed to achieve this and when the deposit occurs on sand, shingle or pebbles the amount of heat necessary to raise the whole to ignition temperature is so great that, in practice, the cost of removal would probably be excessive.
3. The application of an oil-absorbent, combustible material, such as saw-dust impregnated with an oxidant, resulted in a much steadier burning rate and an increased removal of the deposit. The additive, however, burns away before the higher-boiling, tarry fractions begin to burn.
4. Although some improvement was obtained by adding materials which function as a wick, the same limitation regarding the amount of heat to be supplied still operated.
5. A major disadvantage of burning as a method for the removal of oil deposits on beaches, especially when dealing with the large semi-solid lumps, is that, when heat is applied, the oil becomes mobile and penetrates deeper into the beach, thus increasing the contaminated area if it becomes exposed at a later date.
6. On the basis of these small-scale experiments it was considered that, for all practical purposes, burning beach oil deposits would be less efficient and more costly than mechanical or manual removal, and that further investigation would be unprofitable.

Coating of Tarry Deposits

The most widely-occurring type of oil deposit, and the least amenable to treatment with emulsifiers, is in the form of sticky, semi-solid, tarry lumps which can be anything up to one foot in diameter.

A possible method of making these less objectionable and more resistant to splitting and spreading when pressure is applied is to treat them with a porous, powdered solid which would absorb the oil and, with time, become a hard cement-like lump or form a hard skin which would contain the sticky mess. The material used should be such that it is unaffected by sea water.

For the investigation of this technique, some tests were carried out with various powdered solids on oil collected from a beach. Three different methods of application were used. These were:

a. dry dusting;
b. application as an aqueous slurry; and
c. coating and then spraying with water.

Among the materials used were: calcium sulphate (plaster of Paris); Portland cement; a commercial concrete cleanser; calcium oxide; a water-proofed ground limestone; and Fuller's Earth. In dry dusting oil was placed in glass petri dishes, coated with the various dry powders and allowed to stand for 16 hours, after which sea-water was added and allowed to flow over the samples; the condition of the deposits was then examined. In Method b. the materials were made into an aqueous suspension containing 50 per cent by weight of solid and poured over the deposit, which was examined after 16 hours. In Method c. calcium sulphate was used for coating, and, a water-jet used to wash it away, the water-jet on one occasion containing a surfactant. The conclusions from this group of experiments were as follows:

1. The dry dusting of sticky, semi-solid, tarry beach deposits with porous absorbent powders fails to convert them to innocuous lumps which cause no further nuisance. In most cases the powder is absorbed by the deposit which, on contact with water, regains its sticky and contaminating surface.
2. The application of the powder as an aqueous suspension is ineffective in producing a hard coating because of the non-wetting of the oil surface by water. A thin skin is formed with plaster of Paris and a better coverage can be obtained by the incorporation of a wetting agent, although this is accompanied by an increase in the time for setting.
3. In all cases where a surface skin forms, it is easily fractured on impact, exposing the sticky, tarry oil. If left undisturbed, oil seeps through the skin.
4. A disadvantage of this technique is that only the exposed surface of the oil deposit can be treated, so that, if it is subsequently disturbed, which is quite likely

to happen under shoreline conditions, the untreated surface would become exposed.

5. It is considered that as each separate lump of oily deposit would require individual treatment, the time and labour involved, assuming that a satisfactory material and technique were found, would be excessive compared to mechanical or manual methods of removal.

As a result of the negative nature of these conclusions no further work on this method of treating oil was undertaken. It is of interest to note that, after a pollution incident in the Tay estuary in 1968, experiments were made and a heavy deposit of water-proofed limestone dust was found to provide some alleviation on little used foreshores.

Mechanical Removal

Where large quantities of liquid, or semi-liquid oil can be reached by suitable equipment mechanical removal is obviously the most suitable method to adopt. The removal of the top oil-coated layer of a beach material using mechanical excavating or earth moving equipment is also recommended. Machines of this nature are, however, unsuitable for dealing with semi-solid oil deposits. An investigation was, therefore, carried out into the development of a machine for this purpose. It was essential that such a machine should be inexpensive to manufacture so that it could be purchased by small local authorities or those, who might only have small stretches of coast line to deal with.

One idea considered was a machine mounted with a rotary brush unit. It was envisaged that the brushes would collect the lumps of oil from the beach surface. The disadvantages appeared to be the difficulty of combing the oil from the brushes and the severe wear of the brushes on pebble beaches.

Another idea considered was a machine which would scoop the beach up over a width of 2 m and to a depth of 15–20 cm, in some way remove the oil and discharge cleaned beach materials at the rear of the machine. This, being a complicated machine, would be expensive to manufacture and operate, though one has more recently been developed in Germany. It became apparent that the collection of very small oil deposits with much clean beach material was complicating the design, resulting in costly manufacture.

It was considered that a simple spiking system which would pierce the oil lumps, with a combing device for their collection, would be inexpensive to manufacture. This system would obviously not be capable of picking up very small lumps of oil, owing to design requirements, but it was decided to proceed in view of the low cost of manufacture.

After various experiments a unit was made which consisted of a bank of toothed discs; each disc had a 3 inch diameter hole in its center, but ran on a 1¼ inch diameter shaft. The spacing between discs was maintained at 1 inch by welding a short length of 3 inch internal diameter tube to each disc. The combs used with this unit were designed to allow a small amount of movement between the discs, so that any irregularity in the flatness of the discs would not affect the free rotation. This unit was tested and found satisfactory on a pebble beach as it allowed any disc to fall between pebbles and collect up the oil; it was also observed that this system did not pick up many pebbles, very few being collected in the trays.

Three units were built, each consisting of 30 of the toothed wheels mounted on a common axle and each fitted with a separate collecting box for the oil lumps. The three units were mounted so that they could be drawn by a hydraulically-operated forward-mounted boom which was in turn mounted on the front of a Fordson Major four-wheeled drive tractor. The units were mounted onto the boom by towing and lifting chains, retained in position by a simple flexible linkage system and also by two chains attached from the outside of the front units to the rear unit.

A prototype unit shown was constructed for trials and was shown in March 1962 to representatives of United Kingdom Local Authorities and delegates from the Inter Governmental Maritime Consultative Organization, which was in session at the time.

Many United Kingdom Local Authorities possess tank lorries used either for emptying cess pools, or for cleansing street gulleys. The powerful suction which these machines provide can be used readily to remove liquid, or semi-liquid deposits of oil, or water-in-oil emulsion from beaches, providing that the initial layer is sufficiently thick. A number of experiments were carried out in 1969 and it was found that, if the normal heavy duty 5 inch diameter hose was terminated in a length of more flexible suction hose (perhaps 2½ inch in diameter) and the end of this was provided with a suitable nozzle, then a good deal of oil could be picked up. Tests indicated that it was necessary to provide a wire mesh guard to prevent large stones from being picked up, which tended to block the corrugated pipe, and practical experience showed that it was desirable to allow air to be sucked in at the same time.

Emulsifiers

The most common way of removing a deposit of oil, or grease, is to add a suitable emulsifier and then to wash with water, so dispersing the oil in the form of fine droplets, (or an emulsion) throughout a larger volume of water; if the resulting emulsion is stable then complete cleansing results. This, of course, is the normal process of dish washing which is carried out in all sorts of processes throughout the world. It was, therefore, logical to consider whether oil pollution of a beach could not best be dealt with by the use of a suitable emulsifier.

Consequently, in 1960, a large number of laboratory tests were carried out on the emulsification of fuel oil in sea water using a variety of materials. It was soon observed that the application of an emulsifier in the aqueous phase to oil resting on a solid surface was far less effective than if the same amount of emulsifier was applied in a suitable solvent. A program of work was, therefore, planned for the quantitative assessment of a number of different combinations of readily obtainable emulsifiers and solvents for the dispersion of liquid oil pollutants. The procedures and conditions necessary for the efficient removal of liquid oil from samples of beach material were also evaluated.

TABLE 1. EMULSIFIERS AND SOLVENTS

Emulsifiers	Composition
Lubrol G	Blended, anhydrous ethylene oxide condensate
Lubrol PC	
Lubrol MOA	Long-chain fatty alcohol/ethylene oxide condensate with a relatively short polyethylene glycol chain
Lissapol NX	Anhydrous nonylphenol ethylene oxide condensate
APN5	Nonylphenol ethylene oxide condensate
Nonidet P40*	Octylphenol ethylene oxide condensate

Solvents	Saturated hydrocarbons	Unsaturated hydrocarbons	Aromatic hydrocarbons	Oxygenated compounds
Shellspark	77.7	0.9	18.5	1.9
Shell Distillate	83.0	0.7	15.1	1.2
Shell Gas Oil	68.1	9.3	21.1	1.5
Aromasol H	-	-	>99	-
Aromatic Residues	-	-	>99	-
Coal Tar Naphtha * (boiling range 168° to 220°C)	14.5	8.8	68.6	8.1

*The Nonidet P40 and the coal tar naptha were added to the series at a later date.

The first methods used for assessing the emulsification efficiency of an emulsifier solvent mixture were visual inspection, or a lengthy and laborious technique involving the recovery of the dispersed oil by solvent extraction and weighing. A good deal of effort was, therefore, applied to drawing up standard tests at Warren Spring Laboratory, and these have produced reliable and repeatable results. This work has more recently been restarted under the auspices of a Working Party of the Institute of Petroleum and more recent developments in this field are described by Mr. Beynon in another paper in this Conference.

Preliminary experiments on the removal of oil from single large pebbles with samples of the three main classes of the surface active agents (anionic, cationic and non-ionic) suggested that the best dispersion of fuel oil in sea water was obtained with the non-ionic type. Consequently five non-ionic commercially-available emulsifiers were chosen and five cheap, readily available, solvents varying in composition from a predominately aliphatic to a wholly aromatic type were selected to make up a series of formulations. The emulsifiers and solvents used are shown in Table 1.

It was established that all the emulsifiers and all the solvents were completely miscible with fuel oil. It was found, however, that Lubrol PC and Lissapol NX were only slightly soluble in Shell Distillate, or Shell Gas Oil. To make use of these two solvents, they were mixed with an equal volume of Shellspark, when reasonably clear solutions with the two emulsifiers were obtained. An improved solubility was obtained with the Shellspark/Shell Gas Oil mixture if one drop of Lubrol MOA was added. The remaining emulsifiers and solvents were all mutually soluble.

A 10 per cent solution, by volume, of each emulsifier in each solvent was prepared and the resulting cleansers suggested, subjected to tests already devised. Of the formulations tested, it was evident that the combinations of Lissapol NX with one of the solvents containing a high proportion of aromatic hydrocarbons was the most efficient for the dispersion and removal of fuel oil.

The essential desiderata when oil is removed from a beach by dispersion with surface-active agents are that the dispersed oil should remain dispersed when diluted in the sea and not cause recontamination when washed back on the beach. To check whether these requirements were met, a simple experiment was carried out by treating 5 g of fuel oil with 2 ml of cleaner, dispersing the oil by agitation with 200 ml of sea water and pouring the dispersion, in portions, into 2 l of clean sea water. A brown cloud of dispersed oil globules appeared in the water, which became darker as more of the dispersion was added. The oil remained dispersed on standing, a very thin film of oil appearing on the surface of the water. This diluted dispersion was then added to a further 2 l of sea water, good dispersion being maintained. When this was poured through a bed of large beach pebbles no visible contamination of the pebbles occurred. Clean water was poured through the pebble bed and the effluent was almost entirely free from oil. The pebbles caused no contamination when handled and did not mark clean filter paper when pressed against it. It can therefore be concluded that once the oil is dispersed, and the system kept in a state of movement, it remains dispersed when diluted to a concentration of 5 g oil/gallon water or less and would not be deposited on beach pebbles to produce further contamination. This dilution should be readily obtainable under field conditions.

To test these materials, a model beach containing shingle, pebbles and sea water was constructed in the laboratory. This model beach was used to determine the differences obtained when the oil coated with the solvent emulsifier was subject to tidal action alone, or when it was agitated by means of a jet of water. These laboratory experiments were then repeated on a large number of trial patches on various beaches and from this the conclusions reached were:

1. The optimum cleanser formulation for the dispersion and removal of persistent liquid oil pollution from beaches is a ten per cent (by volume) solution of a non-ionic surface-active agent of the ethylene oxide condensate type in a hydrocarbon solvent containing more than 50 per cent aromatic hydrocarbons. The most efficient agent of those tested was found to be Lissapol NX, a nonyl phenol ethylene oxide condensate, and the most suitable solvents were Aromasol H, aromatic residues and a coal tar naphtha fraction of boiling range 168°–220°C, flash point 130°F.
2. Once the oil has been removed as a dispersion in water, if the system is kept in a state of agitation, the oil remains dispersed on dilution with more water and is not re-deposited on beach material.
3. Concentrations greater than 50 p.p.m. of oil dispersed in water with the aid of an emulsifying agent will give rise to a visible surface oil film in a static system.
4. Oil which has been left on a beach for a long time becomes fairly attached to the beach material and is more difficult to remove with surface-active agents than freshly deposited oil. The dispersion method, using the materials studied, is not suitable for semi-solid, tarry deposits.
5. The smaller the particle size of the beach material the more difficult it becomes to remove deposited oil, i.e. large pebbles are cleaned more easily than sand.
6. About 50 per cent by volume of cleanser to oil is required for good dispersion and the best results are obtained if this is distributed in one application. Less satisfactory results are obtained if the contaminating oil is left for several hours before treatment with cleanser or if it is treated and left for several hours before washing with water.
7. Hosing down a treated patch of oil with a jet of water in conjunction with tidal action produces excellent results.
8. For efficient removal of the dispersed oil into the sea a rapid and maximum fall in the water table is desirable. In a beach with a high water table, the dispersed oil tends to separate out on the surface of the water and can become re-deposited in the beach.

It was realized that these chemicals might be toxic to marine life so that, at the same time that the work was being undertaken, the Shellfish Laboratory of the Ministry of Agriculture, Fisheries and Food, Burnham-on-Crouch, was carrying out tests on the toxicity of these materials to marine life. These tests, and later more sophisticated tests, will be described by my colleague Dr. Shelton, of that Laboratory, in another paper in this Conference.

Demonstrations of methods of beach cleaning were given to maritime local authorities in England, Wales and Scotland in 1961 and an explanatory memorandum was circulated.

Oil On The Sea

The problem of dealing with oil when it has landed on the shore is complicated by the different types of terrain; thus the oil may be on sand, shingle, rocks, jetties etc., or on the muddy banks of estuaries, or entangled with reeds or marsh grass. Each of these different types require a different treatment, so it is desirable to be able to treat the oil while it is still floating on the water.

There are four general methods which can be considered:

1. mechanical removal;
2. addition of some material to absorb the oil, or otherwise aid the mechanical removal;
3. sinking the oil by the addition of a material which increases its density; and
4. dispersing the oil in the bulk of the sea.

Each of these methods will now be discussed separately in so far as they have been the subject of Ministry of Technology work.

Mechanical Removal

A number of mechanical devices have been examined by various Ministry of Technology laboratories, but no further work has been undertaken. It would appear that so far no machine or pump has been developed which will work satisfactorily in conditions other than with slight waves and currents. Within these limitations, there are a number of devices which work very satisfactorily.

Addition of Absorbent Material

Floating oil can be partially immobilized and its removal facilitated if it is covered with an absorbent material such as hay, or straw, or an absorbent foam such as polyurethane foam, or even by applying other materials such as treated paper etc. The Warren Spring Laboratory has examined the efficiency of a number of these materials; however, as the Laboratory's work is confined to the problems of the sea, where the collection of any of these materials over a wide area is particularly difficult, no definitive work has been carried out. As a matter of interest, it can be reported that some success was obtained by coating the oil patch with fibrous cobweblike threads of plastic material which are produced and applied by spraying on the oil surface a solution of plastic, e.g. a PVC–PVA co-polymer in a volatile solvent such as acetone. The oil and plastic form a maneuverable raft which can be gathered up manually, or by a simple conveyor system.

This method was tested both in the laboratory and in a dockyard and a provisional patent was applied for at the time (B.P. 11037/62). The major problem which prevented the method from being carried further was the provision of suitable spraying or distribution equipment for the light threadlike filaments under natural conditions.

Mechanical removal has an advantage as it provides a permanent solution of the problem; the oil is physically removed from the polluted area and does not remain in the water.

Sinking

An apparently promising method for the treatment of floating oil is the distribution over the oil patch of a powder, or fine granular solid, of high true density which mixes with the oil, adheres to it, and sinks it. An essential requirement is that the solid should so fix and retain the oil that, once submerged, no oil is released to renew the contamination. Ideally, the submerged mixture of oil and powder should set to a solid mass so that the oil is completely immobilized. In 1961 the Warren Spring Laboratory carried out a number of laboratory experiments on powders of this kind and these were followed in the autumn by trials at sea.

Experiments in the laboratory had shown that a satisfactory way of uniformly spreading a small quantity of powder was to use a pressurized powder sprayer, such as is employed in certain types of fire extinguishers. Two of these devices were used, each of which would take a charge of about 21 pounds of the powdered solid employed, and distribution was affected by pressurizing the cylinder to 75 pound/in^2 with nitrogen gas from a high pressure cylinder. The powder was ejected through a hose with a pistol-type dispenser attached. The laboratory trials had shown that an average coverage of 2.5 pound/yard^2 could be obtained on a rectangular area of 6 yards^2 with the leading edge 6 feet from the jet. Taking as a basis that 60 per cent by weight of powder was required to sink fuel oil, this corresponded to 3 pound/yard^2 assuming an oil thickness of 0.1 inch.

The materials which were found to be more satisfactory in the laboratory tests were used; these were screened builders' ballast, commercially available silver sand, crushed clinker and crushed brick. All the materials were quite dry and passed through 25–72 mesh size. The procedure was to approach the oil slick slowly and, making allowance for the effect of wind, to spray the powder onto the oil with maximum coverage. The time taken to discharge one sprayer was between 30 and 60 seconds. A marker buoy was thrown overboard in the area of the test so that no two tests were carried out over the same spot. In each case one gallon of oil was discharged and attempts were made to sink it. The work was carried out some half a mile from shore, but in an area where the sea bed was dry at low tide. It was therefore possible to go out on the flats and, by finding the buoy, discover whether any of the sunken oil was on the sea bed. In only one case, sunken oil was found and small streaks of oil were observed in nearby water pools. This was taken as showing that some success was achieved using sand. These early experiments were particularly useful as they demonstrated the great difficulty of spreading a fine dry powder over any considerable area under normal wind conditions. It was calculated that for these light slicks, it might be necessary to use up to 100 pounds of the sinking agent to sink 10 pounds of oil. The evidence of what happened to the oil after being sunk was incomplete; it was believed that a good deal of it was carried away by the tide. At the same time, the Burnham-on-Crouch Laboratory of the Ministry of Agriculture, Fisheries and Food, which had been associated with the Warren Spring Laboratory in all of the oil pollution experiments where there could be hazard to sea life, carried out limited tests from which it was decided that there was a considerable danger of trawling or other bottom fishing gear being contaminated by sunken oil, and it was pointed out that the sinking would have to be avoided in the vicinity of beds of oysters or other shellfish. Consequently, at this time, no further work on the sinking of oil was carried out.

Laboratory tests on the efficiencies of various powdered solids, using a simple agitated system to simulate in some way the action of waves, were tried on a number of materials. The results are shown in Table 2.

At the time of the *Torrey Canyon* a great deal of publicity was given to the fact that the French were able to sink oil using a stearate treated powdered chalk. It should be pointed out, however, that the French marine biologists were well aware of the danger of contaminating fishing grounds by sunken oil and therefore, all of the oil was sunk over the edge of the Continental Shelf, very largely in water exceeding 1,000 feet deep. The oil too was not crude oil as spilled but had been converted by a combination of aging and the action of the waves into a water-in-oil emulsion; this was in fairly large agglomerations having a density closely approaching that of sea water. It was, therefore, found possible to sink these oil patches by the manual application of the chalk material directly emptied from bags onto the oil floating on the sea. When more sophisticated means of spreading the powder were tried, grave difficulties arose due to the clogging of essential parts of ships' gear and equipment. The Warren Spring Laboratory is therefore carrying out a new series of experiments and tests on the use of sinking agents.

The first series of experiments was designed to assess the qualities of various sinking agents for three separate parameters under as nearly reproducible conditions as possible. These parameters are:

1. *Oil Retentivity*, or the amount of oil that a given weight of sinking agent will maintain sunk for a given period. Clearly some time limit must be imposed and, for these tests, a period of 24 hours was selected.

2. *Oil Water Affinity Index Ratio*, a measure of the relative affinities that the material has for oil and for water.

3. *Sinking Weight*, or the weight of sinking agent required to sink a known amount of oil floating on a sea water surface. This is invariably different from the oil retentivity as the freshly sunken oil-mass tends to bleed oil until it reaches some sort of equilibrium.

The first test examined the effects of the particle size or surface area of the grains of material on the oil retentivity.

A bulk of large quartz fragments was roughly crushed and sieved to give a quantity of about 1 kg in each of a series of size fraction.

Samples from each size fraction were treated with different coating materials: silicone oil M.S. 1107, made by Midland Silicones Ltd; and three long chain aliphatic amines, Armac T, Duomac C and Duomac T, supplied by Armour Hess Ltd.

TABLE 2. EFFICIENCY OF POWDERS FOR SINKING FLOATING OIL

Material	True Density g/cm^3	Quantity used, % by wt of original oil	Amount of oil sunk, % (visual inspection)	Remarks
"Oilsink"	3.26	50 - 60	100	Oil remained submerged.
Portland Cement	3.42	70	85	Some oil released on standing.
Fuller's Earth	-	100	Nil	Powder absorbed the oil.
Plaster of Paris	2.77	100	50	Oil began to sink after the addition of 70 per cent.
"Magnus IDX"	2.38	60	95	Of the sunken oil, 40 per cent was sunk as lumps and the remainder was dispersed and carried down with the flocculent precipitate formed.
"Baribux" Waterproofed Ground Limestone	2.81	60	95	The remaining 5 per cent of oil required another 40 per cent of powder to sink it.
Gravel (14 B.S.S.)	2.71	80	100	Some oil released on standing.
Gravel (-14 B.S.S.)		80	60	As the oil film became thinner when oil was removed by sinking, the gravel broke through the film and sank without carrying any oil with it.
Powdered Coke	1.87	40	50	Further addition of coke did not admix with the remaining oil and was rapidly washed off into the water.
Bentone 34 (An organophyllic clay)		60	Nil	The oil rolled up into leathery lumps. Density of powder probably too low.
Calcium Carbonate		100	50	-
Calcium Oxide		80	5 - 10	The oil was slightly dispersed on the surface.
Refractory Brick (<25 B.S.S.)	2.27	50	98	No oil released after 3 days standing
Red Brick (<25 B.S.S.)	2.69	70	95	-
Yellow Brick (<25 B.S.S.)	2.65	50	95	-
Clinker (<25 B.S.S.)	2.60	50	100	No oil released overnight
Earth (<25 B.S.S.)	2.49	50	70	-
Mixture of Equal Parts of Portland Cement and Magnus IDX		100 70	95 95	Oil was dispersed and carried down with the powder and ppt. Not as good as Magnus IDX alone.
Mixture of Equal Parts of Portland Cement and Plaster of Paris		50 70	70 95	-
Mixture of Equal Parts of Portland Cement and Bentone 34		50 70	Nil Nil	Half the oil floated as leathery lumps and half floated as a surface film.
Mixture of Equal Parts of Portland Cement and Gravel (<14 B.S.S.)		50 70	90 95	All sank at first but about 10% rose to form a surface film. Addition of a further 20% again sank it all but 5% rose to the surface.
Sand (18-25 B.S.S.)		40 60	60 90	
Sand (36-52 B.S.S.)		40 660	90 90-95	Initially all the oil was sunk at both sand concentrations, but oil was released on standing.
Sand (72-100 B.S.S.)		40 60	90 95	
Sand (<120 B.S.S.)		40 60	70 70	

TABLE 3. CRUDE OIL RETENTIVITY (24 h) OF UNTREATED AND TREATED SIZE FRACTIONS OF SAND

Mesh Size B.S. Sieve	Surface Area m^2/g	ml of Crude Oil Retained by 10 g				
		Untreated	Silicone	Armac T	Duomac C	Duomac T
− 6 + 10	0.09	2.9	3.4	3.1	2.5	0.5
− 10 + 14	0.08	2.9	3.7	4.2	3.4	0.6
− 14 + 25	0.08	3.7	4.7	4.6	3.7	0.8
− 25 + 36	0.10	3.8	4.4	4.8	3.6	1.3
− 36 + 52	0.10	4.7	4.7	4.9	3.8	1.8
− 52 + 72	0.16	5.0	4.3	5.2	4.0	1.8
− 72 + 100	0.14	5.0	4.3	6.3	4.2	4.2
−100 + 200	0.29	5.0	4.2	6.3	4.4	4.4
−200 + 300	0.49	5.0	4.4	6.2	4.9	4.4
− 300	0.78	5.2	4.7	6.9	4.7	4.5

10 g of the sand sample was weighed into a 250 ml beaker, 10 ml of crude oil added and the whole mixed thoroughly. 200 ml of synthetic sea water was added and the beaker and its contents allowed to stand at room temperature for a period of 24 hours. At the end of this period the sea water together with the floating oil was decanted off from the sunken oil mass and discarded. All the oil adhering to the sides of the beaker was wiped away with a tissue and discarded. Finally the sunken oil was dissolved out of the sand and determined absorptiometrically. It was found that the oil retentivity of sand increases as the grain size decreases, and hence as the surface area increases, up to a certain limiting size. This size is about 100 mesh B.S.S. Using sand below this size does not appear to have much effect in increasing oil retentivity. Treating the surface of the sand to render it more hydrophobic and more oleophilic produces some change. With the exception of the Armac T treatment, it reduces the oil retentivity of the sand by a small amount, but with Armac T, the oil retentivity shows a marked improvement. The results are shown in Table 3.

The oil-water affinity index ratio was adapted from a method for the measurement of the adhesion tension of liquids in contact with powders developed by V.T. Crowl and W.D.S. Wooldridge.

The rate at which oil rises up a tube packed with the solid by capilliary action is compared with the time taken for water to rise up a similarly packed tube.

From these figures and the viscosity of the two liquids a figure called the oil-water affinity index ratio (OWAIR) was calculated and the results obtained from a variety of materials are shown in Table 4.

The OWAIR value is shown as fraction x/y where x and y are the oil and sea water parts of the fraction respectively. Thus if x and y are both large numbers, then the material has a great affinity for both oil and water. But if x is high and y is low, then the material has a much greater affinity for oil than it has for water. If x and y are both low, then the material has little attraction for either oil or water. Thus it is seen that untreated sand is wetted preferentially by sea water, while stearate treated sand and waxed sand have no great affinity for either oil or sea water. Silicone treated sand and Armac T treated sand, however, both have a much greater affinity for oil than for water.

It was hoped that experiments on the weight of solid required to sink oil would give reproducible answers. However, this was not so, but the results are included as they give some indication of the behavior of various sinking agents.

The action of sinking a slick of residual oil does not appear to depend solely on increasing the resultant density of the mass until it is greater than the supporting liquid. On adding a sinking agent, the slick becomes saucer shaped and does not sink until water laps over the edge and fills the center depression, by which time the density is usually considerably greater than the sea water. This effect is reduced in natural conditions with wave action, but these conditions are difficult to reproduce in a laboratory on a small scale. In these experiements of 50 ml of Kuwait oleophilic residues floating on sea water was sunk by sprinkling the sinking agent on to it by hand.

TABLE 4. OIL WATER AFFINITY INDEX RATIO (OWAIR) OF VARIOUS SINKING AGENTS

Sinking Agent	OWAIR
Plain sand	28.9/37.3
Armac T treated sand	29.6/3.9
Duomac C treated sand	38.5/12.5
Duomac T treated sand	36.0/11.6
Silicone treated sand	33.9/0
Silicone treated P.F.A.	3.9/0
Waxed sand	1.1/0
Stearate treated sand	0/0
Stearate treated whiting	1.1/0.1
Stucco	4.6/31.7
Polyphant Stone	28.1/11.2

TABLE 5. SINKING WEIGHT OF VARIOUS SINKING AGENTS

Sinking Agent	Weight to sink 50 ml oleophilic resid.
Plain sand	27.8
Armac T treated sand	29.2
Duomac C treated sand	31.1
Duomac T treated sand	28.4
Silicone treated sand	43.6
Attapulgite	34.4
Waxed sand	34.6

The results are shown in Table 5. For the sample of plain sand and Armac T treated sand, 12 determinations were made on each sample. The maximum divergences from the mean of these two samples were 4.7 on 27.8 and 5.0 on 29.2. On the other samples 4 determinations were made.

Considering the divergency of the determinations, it would appear that treatment of the surface of the sinking agent has little effect on the weight of material required to sink a given weight of oil.

Although the Laboratory results were far from conclusive, it was felt that yet another experiment should be carried out at sea on the distribution of fine powders to sink oil, and also a test of hypothesis that fishing gear may become fouled if a trawl is made over the area. With these problems in mind, the Fisheries Laboratory at Burnham-on-Crouch and the Warren Spring Laboratory combined in an experiment which took place in an area of the Thames Estuary known as the Maplin Sands in September last year (1968). Arrangements were made to empty 45 gallon open topped drums of crude oil over the side of a fishing vessel. The powder was distributed over the oil using a pipe 14 feet long and 2 inch diameter pierced with 20 holes; the powder was pumped through a Type P12 Monopump and fluidising air was passed both through the bed of the feed hopper and on the delivery side of the pump. The material used was Snowcal CW1 activated whiting.

At the time of the experiment, the weather was fine and there was scarcely a breeze. The powder equipment functioned perfectly, all 20 jets blew out powder and a long white plume trailed behind the boat and hardly appeared to touch the sea. However, when the ship turned about and headed into the wind, it was enveloped in a choking white fog. This method of discharging air entrained powder was therefore concluded to be quite impractical. Although large white patches remained on the surface of the sea the powder did however seem effective in dispersing the oil.

A similar experiment was carried out in which the whiting was pumped out with water as a slurry; in this case, some of the powder was still dry and blew about as the water jet hit the sea. Although the jet tended to penetrate the surface, a considerable mat of powder remained floating.

A subsidiary experiment was also carried out using fine sand treated with an amine; this was less satisfactory as the method of distribution appeared to discharge the slurry straight through the oil surface without carrying the oil down with it.

The area in which the oil had been sunk by the chalk was then fished over by the Ministry of Agriculture, Fisheries and Food research vessel *Jassa* which carried out a series of hauls with a 15 foot beam trawl and a standard 3 foot sledge oyster dredge. In five hauls, few small fish, crabs and shells were collected but there was no sign of oil on any part of the gear. It was considered that in view of the small quantity of oil, the tidal movement, and the difficulty of marking, the test was not conclusive.

Early in 1969, a report was seen of a German invention in which oil absorbing materials were dropped onto the sea in sacks made of water soluble polyvinyl alcohol; small scale laboratory experiments with this material were then made. Small bags were made of polyvinyl alcohol film and filled with: a. stearate treated chalk; and b. siliconised pulverised fly ash. The bags were dropped from a height of two to three inches into small pools of oil contained in a beaker. The bag in each case sank immediately, becoming coated with oil as it passed through the slick, and carrying the oil to the bottom. After two or three minutes the oil on the bag started to float to the surface, leaving clear patches of film exposed to the sea water. These patches rapidly softened and slowly peeled back, leaving a block of powder on the bottom in the same shape as the bag. In neither case did the powder rise to the surface unaided; prodding the block with a stirring rod did not cause any flotation of the material, but it was possible to manipulate small pieces to the surface. Although in theory it might be possible to include enough air in each bag so that the bag filled with the material floated on the surface, as a coating of oil on the polyvinyl alcohol prevented the attack of the sea water so that the bag did not dissolve; it was, therefore, felt that this method did not justify any further work.

The Shell Company, in Holland, reported that they had had considerable success with sinking oil with sand treated with an amine. Visits were paid by Warren Spring Laboratory staff to the Dutch Shell Laboratories and full information was given about the methods which they had used. In view of the highly favorable results which had been obtained, it was decided to repeat the Shell experiments on the open sea under conditions in which trawling could take place over the sunken oil. A British Admiralty experimental vessel was, therefore, obtained and arrangements were made to carry out the experiments in May 1969 off Portland in the South of England. In these experiments, local soft sand was treated with an amine 'Armac T' and used to sink two sorts of oil, the first, topped Kuwait Crude; and the second, fuel oil of 2,000 sec^{-1} Redwood. To avoid any potential fouling of the local sea and coast, the oil to be sunk was enclosed between two floating booms which were drawn past the vessel underneath the discharging nozzle. A mixed team of skin divers, consisting of Naval personnel and marine biologists, was used to observe the oil actually sinking and to examine the condition of the sea bed after the oil had been sunk.

A full scale experiment was conducted using 40-45 gallons of the fuel oil. The skin divers were able to observe the material leaving the surface which they described as thread-like slivers and not lumps (it should be explained that sea water was applied with considerable force and had the effect of tearing up the slick into thready pieces; these were the bodies seen sinking by the divers). On the bottom, discrete lumps or threads were not observed, but a silk-like deposit was reported and this was oily to the touch; presumably the threads broke up on the way down. Sinking appeared to be rapid and vertical, it being slack tide. At most, 60-70 per cent of the fuel oil was sunk by the same treatment and there was no direct evidence that the oil was released to the surface. As soon as the oil had been sunk, the trawler which was standing by was asked to trawl through the sunken area which had been marked with buoys by the divers.

A small 2-inch mesh otter trawl with 3-inch bobbins on the ground rope was then fished through the sunken material, which was lying on a fine sand bottom. When the net was hauled, it was apparent that small patches on the underside of the trawl were fouled by a thin coating of heavy fuel oil. There was no question of any of the meshes of the net being blocked by oily lumps since the fouling was only present as an oily film up to 2mm in thickness on the net fibre. Each patch comprised from 2 to about 5 meshes. The otter boards and ground rope were unaffected by oil and most of the oily patches were observed on the fore belly within about a half meter of the foot rope. Occasional traces of oil were present on the after part of the belly but the cod end was free of fouling. This was quite possibly due to the fact that the under side of the cod end was protected by rubber sheeting cut from motor car innertubes. The catch consisted of one cuttlefish, one plaice, two skate and two dogfish. None of the catch appeared to be fouled while in the cod end but when examined on deck one of the dogfish had two patches (thin smears) of oil about one centimeter square on its skin. It was thought that this was not caused while the fish was in the cod end but during handling on deck.

Considerable practical difficulties were found in carrying out the experiment; nevertheless, a number of conclusions were reached:

1. The sinking was not as effective as first hoped and it would appear that the thickness of the oil film is an important factor. Nevertheless, between 50 and 70 per cent of the oil put on the sea was sunk.
2. The skin divers reported that the oil sank to the bottom in small particles which were only slightly more dense than the sea. Consequently, the tidal current along the sea bed was sufficient to carry the oil over the ripples of sand on the bottom.
3. Trawling was carried out and although no actual lumps of oil were collected, sufficient oil was rubbed onto the netting of the trawl to foul both the catch and the fishermen when they were pulling it back into the vessel.
4. The oil which remained afloat was particularly difficult to dispose of using either more sand slurry or the normal solvent emulsifier mixture agitated by water hoses. Further investigations on this particular phenomenon are being carried out both in England and in Holland.

The opportunity was taken to sink a further amount of oil using stearate treated chalk. In this case the chalk was discharged in large quantities onto the oil floating in the boom and very satisfactory sinking was achieved. Nevertheless when this was trawled through, large lumps of chalk containing oil were retrieved from the sea bed, fouling both the nets and the catch made by the trawler. In both cases, sinking with sand and with chalk, the skin divers were able to bring back small samples of the oil from the sea bed. With sand, the oil still had every appearance of being oil and the amount of sand did not seem to be very great; with chalk, comparatively dry chalk with oil embedded in it was brought from the bottom. The tentative conclusions reached from both of these sinking trials are that although the sand sinking method appears to very desirable, there will be a number of cases in which it should not be carried out owing to the danger of contaminating bottom fishing grounds, shellfish beds, or fish spawning areas.

One of the unknown factors is the fate of oil sunk to the bottom. It is believed that this is subject to bacterial degradation. To find more details of this process, a contrast has been placed by the Warren Spring Laboratory with the Microbiological Department of the University College of South Wales, Cardiff, to find out the mechanism of microbiol degradation. This is a two year contract, and the first year has just been completed.

Dispersal of Oil in the Sea

It would appear that one of the major factors in removing oil from the sea is by bacterial attack. Bacteria can only attack the surface of the oil, so that the bigger the surface area, the more rapid the decomposition of the oil. The effect of breaking the oil up into droplets, or an emulsion, is to greatly increase the surface area and this suggests a satisfactory way of dealing with pollution by floating oil. The Warren Spring Laboratory carried out experiments in 1961 using the same solvent emulsifier mixtures which they had found effective for cleaning beaches. It was found that this produced a relatively quick and satisfactory means of dealing with small scale spillages.

It was found that dispersal consisted of two separate processes: firstly, applying the dispersing or emulsifying agent to the oil and then agitating the treated oil with water so as to produce an emulsion or dispersion. This same agitation mixed the small oil particles into a large volume of sea so that they were apparently less likely to meet and recombine: and as they only rise slowly to the surface, there was less likelihood of their reforming into a coherent film. It was, of course, realized that these materials were likely to be toxic to marine life; nevertheless, in view of the immense dilution which can take place in the sea, this was not considered to be a hazard in open water.

It is perhaps of interest to note that despite the very large quantities of the toxic solvent emulsifier mixture which were used around the Cornish coast at the time of the *Torrey Canyon* incident, no reduction in the total weight of fish caught was observed, nor was there a reduction in the weight of crabs, shellfish etc. landed in the two subsequent years. It can therefore be assumed with a fair degree of certainty that no effect was produced by the use of these materials; nevertheless, it must be emphasized that they are quite unsuitable for use in fresh water, rivers, lakes, etc. or where there is not an adequate amount of sea, such as in estuaries, over shellfish beds, spawning grounds, etc.

A good deal of work by various companies throughout the world has been carried out on developing less toxic emulsifying materials and several have been produced on both sides of the Atlantic. It is particularly difficult to test these materials and as a result, many exaggerated claims for success have been made. Recently the Warren Spring Laboratory carried out a number of experiments in an endeavour to form a more definitive idea of the success of these various materials. The procedure adopted has been to discharge oil through a number of small orifices to produce a relatively uniform sheet of a known thickness of oil on the surface of the sea; this slick is produced by a boat moving into the wind so that the slick is not distorted by wind action. Immediately behind the boat producing the slick is a second boat provided with spraying equipment; a boom can be arranged to spray the dispersant chemical accurately over the width of the slick at any required rate. Dispersion into the sea is then carried out either by water jets directed from a second boom, or alternatively from a fire hose moved to and fro across the slick. A third boat carries observers, who can assess the effect of the emulsification. The oil slick is discharged at a constant rate, but the amount of the chemical under test can be increased, or decreased, until the observers agree that the slick has been dispersed. This affords a fairly reliable way of comparing different materials; these experiments are in progress at the time of writing.

Ignition and Combustion *in situ* of Oil in Wrecked Oil Tankers

Following the wreck of the *Torrey Canyon* and the subsequent report of the Official Committee of Scientists, it was suggested that under certain circumstances it might be desirable to fire the oil contents of wrecked tankers which could not be removed by other means. Consequently, the Rocket Propulsion Establishment was invited to consider this particular problem. It has three main aspects:

1. the reliable and convenient ignition of the oil in the tanks, or on the sea;
2. the type and degree of venting of cargo tanks required for the maintenance of combustion within them at an effective level; and
3. the factors which affect the degree of combustion of oil when burning on the sea.

A survey of the literature suggested that although there was useful background information, the problems were poorly understood in scientific terms; in view of the limited time available, the investigation was made on an ad hoc basis.

Nearly 50 burning tests were carried out in square section tanks of three sizes of up to 1 m^2 cross-sectional area. Crude oil was used in the majority of the tests, but some burnings were also performed using F80 fuel oil. The tanks used had apertures in one side and in the lid, and these were varied from 7 to 50 per cent of the tank cross-sectional area. Burnings were carried out in still air, and in fan generated winds of ~ 6 and ~ 11 m/s. The burning rate and percentage consumption were measured in each test, and the temperatures at various points in the tanks were continuously recorded.

The main findings were as follows:

1. Direct observations, and study of 24 fps cine film records, showed that ignition of crude oil by a small gas-air burner was effected in 1-2 s, even at 0°C. Within 10-15 s the fire had reached full intensity. Ignition of fuel oil (at 15°C) took 5-10 s, and full intensity was reached in approximately 30 s.
2. The burning rate of crude oil was virtually independent of the percentage burnt except for very high consumptions (85 per cent) when a marked decrease was observed. There was an increasing amount of smoke as burning proceeded. Over 90 per cent consumption was achieved in many tests, although in some tests in the largest tank a layer of coke formed on the oil surface, and caused premature extinction.
3. No significant increase in burning rate above that obtained for side and lid holes of equal size was achieved by enlarging either hole. Use of side and lid holes of equal size is thus close to an optimum condition. The burning rate was substantially the same whether the lid hole was adjacent to or distant from the side contaning the hole.
4. Increasing the side and lid hole areas above a certain size (about 25 per cent of the tank cross-sectional area) gave no significant increase in burning rate.
5. The still-air burning rates could be at least doubled by an 11 m/s wind. The increase was greatest for the smallest tank. There is some reason to think that stronger winds would not effect any substantial further increase in burning rate.
6. Under comparable conditions, linear burning rates were greatest in the largest tank. The highest burning rate achieved in still air was 96 mm/h, with 22 per cent side and lid holes. In an 11 m/s wind this rose to 200 mm/h. It is thought unlikely that burning rates of more than 1.5-2 times these figures could be achieved in very large tanks under any conditions of wind and venting hole sizes.

A more detailed analysis of the data is in progress. Empirical scaling rules will be obtained for tentative prediction of burning rates in large (i.e. tanker sized) tanks. Because of the extended extrapolation, the impossibility of scaling some factors, and the likelihood of changes in the physical mechanism of burning in large tanks, the confidence which can be attached to such unsupported extrapolations will be rather low. It is essential, therefore, that one or two burning tests under representative conditions should be performed in a large tank (e.g. a cube of 7 m side) in order to verify the predictions.

The major practical difficulty in applying the results of the study to an actual burning in a tanker is likely to be the problem of creating the side and lid venting holes. The use of plastic explosive, and other techniques more precise than aerial bombing or torpedoing, is under consideration.

Booms

In recent years much thought and ingenuity has been given to the design of floating barriers and similar devices for the prevention of the spreading of oil on the water surface. Probably the greatest incentive to inventors was brought about by the *Torrey Canyon* disaster in March 1967.

The floating oil boom has been a standard piece of equipment in oil docks for many years, and it is because many of the oil terminals are sited in sheltered waters that the design of booms has called for little more than simple buoyancy tubes to encircle a ship during transfer operations. Most of the larger oil terminals possess one or more of these devices to arrest the spread of oil in cases of accidental leakage, but on at least one occasion when a spillage has occurred, the boom has had to be cut free to avoid the fire risk involved with a ship surrounded by oil accumulating within the barrier. The conclusion may be drawn that while the boom is effective in preventing floating oil from spreading in relatively calm waters, a further problem has been created.

The use of the 'conventional' oil boom as a device to contain oil in the open sea met with complete failure off the Cornish coast after the *Torrey Canyon* incident. A number of different types of boom were moored off the coast, but they either broke up completely, or were driven ashore because of inadequate mooring. As a result of the failures of so many moored boom installations in the open sea, it was thought that, in the comparative calm of the neighboring estuaries, the booms might have had a better chance of success, but even in the more sheltered sites little improvement in performance was realized. The failure of booms on the Cornish coast was repeated some weeks later when *Torrey Canyon* oil began to arrive on the French coast at Brittany.

The Hydraulics Research Station had the opportunity of seeing many of the booms laid after the *Torrey Canyon* disaster, and while there was little time to carry out any practical on-the-spot tests, some model experiments were performed in the laboratory to examine the basic requirements for a boom giving satisfactory performance in waves and currents. As a result of this work with models and the experience gained in the field, the Hydraulics Research Station undertook full scale field trials on a number of booms in order to assess their limiting performance, under the natural conditions of a tidal estuary.

The prime object of a floating boom is to influence the flow of surface water in such a way as to hold back the polluted upper layers. It is, however, impossible to forecast accurately the mooring forces experienced by a boom and the degree of deformation of the boom also depends on its position. While the laying of a boom across an estuary to prevent the intrusion of an oil slick from the sea would appear to be best sited at the narrowest part of the river, it is also the region of the highest flow and should be avoided. A boom laid at 90° to the flow will not maintain the desired shape and will bulge at the center of the river where the flow is strongest. Thus the oil will be collected at the center of the stream where it is difficult to remove, and it will flow seawards on the following tide. In practice, the plan configuration of the boom layout should be arranged to deflect accumulated oil to the sides of the channel where it may be recovered mechanically or destroyed by chemical means.

A recommended alignment for a boom whereby all floating matter is deflected to the side of the stream is shown in Figure 1. It resembles a chevron made up from two separate boom lengths. Once concentrated at the inshore end of the boom, the oil may be soaked up in floating straw. The advantage of the chevron configuration is that while the seaward extremity can be closed to prevent incoming contamination, it may conveniently be opened to shipping on the ebb tide, as the moorings allow the boom to swing away towards the banks on either side.

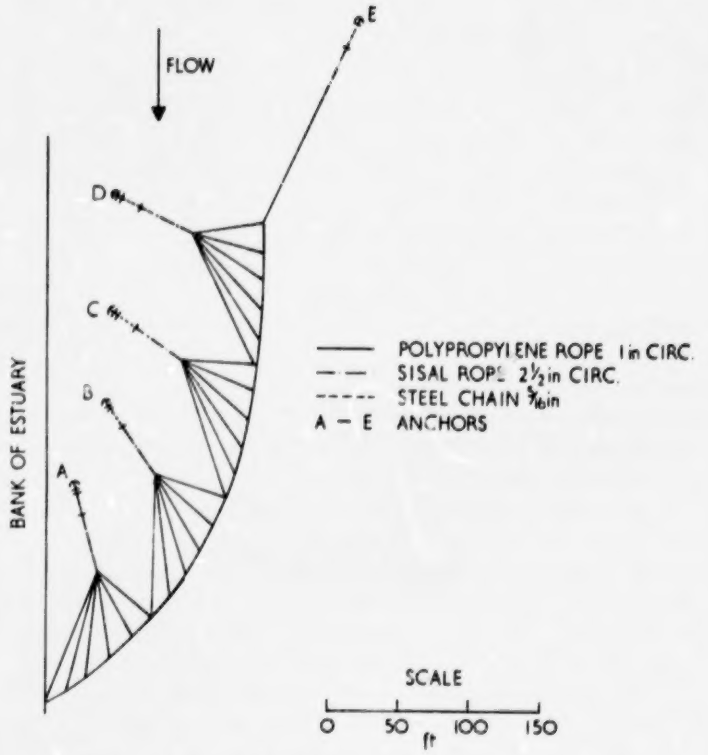

Figure 1. Boom alignment and mooring configuration.

The Hydraulics Research Station invited a number of firms to participate in a test program in the field. For the tests each firm was asked to provide a 400-foot length of boom of its own manufacture. The objects of the test program were as follows:

1. to establish the most effective alignment of a boom to the current;
2. to find a satisfactory mooring arrangement;
3. to measure the mooring forces;
4. to assess the general performance of the booms in stopping floating material;
5. to observe the degree of overtopping; and
6. to suggest modifications to improve performance.

After inspecting a number of sites, one at Newquay called the Gannel was selected as being the most suitable; this has a tidal range of approximately 10 feet during Spring tides and at high water the maximum depth is 12-13 feet above sea bed level in the center of the channel. Current velocities, measured in the center of the river approach a maximum speed of 5 ft/s on a spring flood tide; at low water, there is a hard sand bed which facilitated the handling of booms and their moorings. In some cases, the moorings were laid by the manufacturers to their own design, but in all tests the offshore end of the boom was between 120 and 150 feet from the South bank of the river, and the inshore terminal was a common point for all tests (Figure 2). The boom tests took place at fortnightly intervals, when consecutive high tides offered the most suitable conditions.

As might be expected, the booms showed widely different characteristics; the worst arrested floating material up to a current velocity of 1 ft/s, while the best had a limiting velocity of 4 ft/s.

One of the most significant results of the tests was shown in the advantages to be gained from mooring the booms along their lower edge. The merit of the chevron mooring configuration is that it causes the boom to deflect, rather than to obstruct, the surface flow and it is doubtful if any of the booms would have retained surface floating particles at velocities above 1 ft/s had they been placed at 90° to the flow. Conversely, if the angle made between boom and shore is further reduced, a higher performance would be obtained, but the increase in length of the boom, and consequently the higher costs involved, would make such a layout impracticable.

Although no direct relationship between mooring forces and current velocities could be established, those booms with an effectively deep skirt gave rise to the higher forces. Figure 3 shows typical mooring forces throughout a test period with Type E boom. It will be observed that the terminal moorings are most heavily loaded, while the intermediate array contribute little more than a steadying influence on the shape of the boom by keeping it in a smooth 'arc.' The combined terminal forces exceeded 1 ton, whereas the remaining 3 anchors contributed a total restraining pull of about 200 pounds. Though small, the contribution of the intermediate anchors were important and necessary. In two instances, long sea swell entering the estuary caused the boom to oscillate up and down the channel. Under such conditions, all mooring ropes were brought intermittently into the system and helped to reduce peak loads on the terminal moorings.

Generally, it may be said that the heaviest booms, which were also the most difficult to handle, were more effective in collecting floating material and deflecting it to the side of the river. This statement is true for natural estuaries and channels having a sloping beach or, for other reasons, experiencing lower velocities at the sides of the channel. If the entrance was deep throughout its cross section and high velocities were maintained right across its full width, then it is doubtful whether the desired effects would be achieved, as the surface flow at the inshore ends of the boom would be high irrespective of the angle at which the boom was laid. However, there are many tidal estuaries of the former type where booms could be effective.

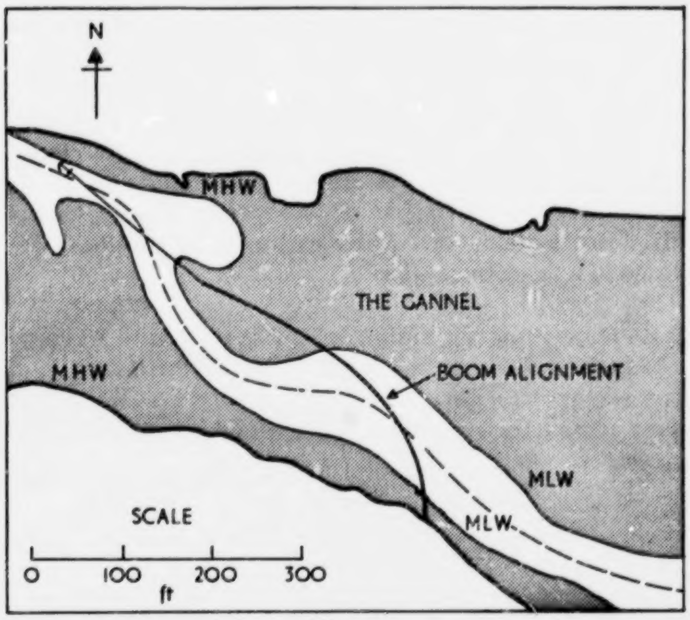

Figure 2. The test site.

To summarize the foregoing, the use of booms is limited to sites where the water velocity of the stream does not exceed 4 ft/s and the selection of the most suitable type of boom will depend on the characteristics of the site and of the method of deployment. If the boom can remain afloat at all times and be towed to the required position in emergencies, then much of the labour and manhandling can be avoided. The use of booms off open beaches and in exposed conditions is unlikely to meet with success. This is because a boom can only cope effectively with long period swell. Under such conditions a flexible boom rides well on the water surface. In short sea 'chop,' however, the wave crests break on the boom and water and oil can over-top the barrier. The effects of long and short wave action were studied in model tests in the laboratory in 1967 and no offline solution was found to the problem.

The Discharge of Oil from Ships

The Warren Spring Laboratory is advisor to the British Delegation to the Inter Governmental Maritime Co-operative Organisation. It became apparent in 1964 that it was desirable to examine the pollution produced by the discharge of the maximum statutory permissible limits of 100 ppm of permanent oil in the ballast water discharged by a vessel. Arrangements were, therefore, made to equip a suitable Naval auxiliary vessel so that it could discharge a precisely known amount of oil into water which was being discharged at a rate of 100 tons per hour. The oils discharged included crude oil, heavy bunker oil, lubricating oil and light marine diesel oil; the rates were varied between 25 ppm and several thousands ppm. It was hoped to be able to discharge all of these under calm, medium and rough sea conditions. However, in the time available it was not possible to complete the full program, but sufficient information was obtained to make the results most satisfactory.

All the discharges were examined and photographed by an observer in a helicopter at various heights above the slick discharge. A number of subsidiary experiments were carried out in which the speed of the vessel was varied and in which oil was discharged with and without the accompanying water. From these experiments it was concluded that emissions of oily water at a rate of 100 tons per hour can be clearly seen from the air, and concentrations down to 50 ppm, or even lower, depending on the conditions of sea and light.

Under all the conditions experienced during the trials, emissions of the order of 100 ppm could be seen as a continuous coherent slick, or trail, at heights of up to several hundred feet, although at heights of 3000-5000 foot emissions as low as 1000 ppm were not always clearly visible. It was also determined that concentrations of oil in the water discharged had no bearing on the visibility of the resulting slick. The visibility was determined by the final surface concentration of the oil on the sea and so it can be

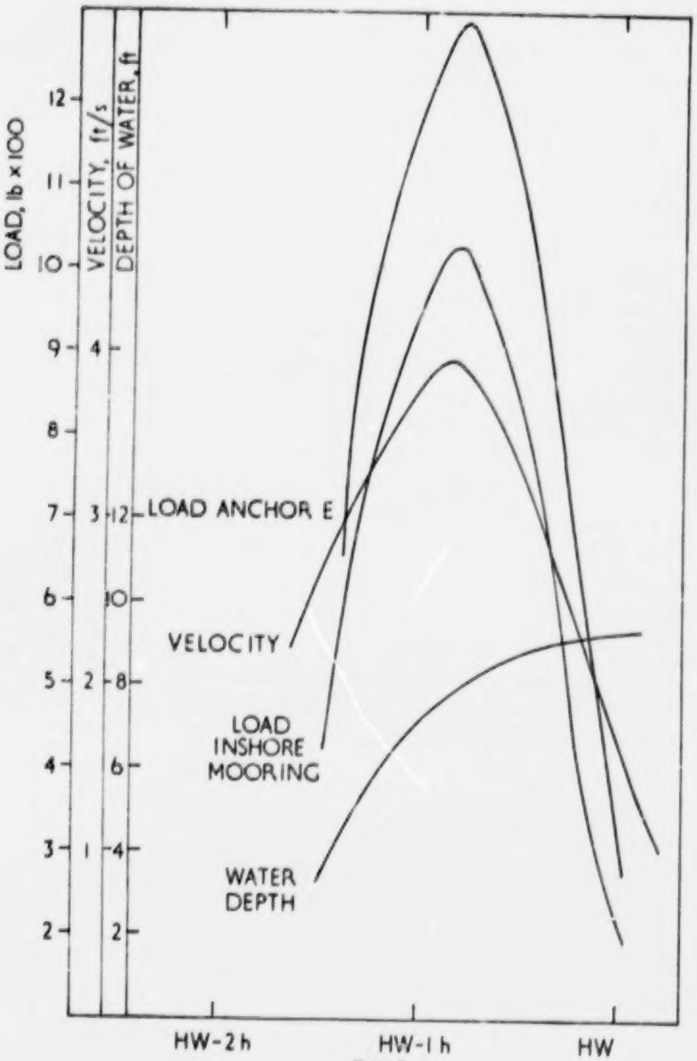

Figure 3. Water depth, anchor load and velocities, anchor E and inshore mooring type E boom.

related to the actual amount of oil discharged for unit distance of the ship's travel; this limit might be expressed as a rate of discharge per velocity, or pounds of oil per foot of travel. It was also determined that finely divided solids suspended in the discharge water produced a slick which could be mistaken for an oil slick where observed from the air by an unskilled observer.

These experiments were discussed with Board of Trade officials and with representatives of the oil companies and the Chamber of Shipping. The advent of the 'load on top' system of tanker operation meant that, under certain conditions of discharge, the amount of oil discharged by a tanker was in excess of 100 ppm, but it need never exceed 2 feet^3 oil/mile of sea traversed. Consequently the Warren Spring Laboratory, in collaboration with the Chamber of Shipping, carried out in November 1968, carried on further experiments off the Pembrokeshire coast to determine the effect of producing slicks of this type. In this case an 18,000 ton tanker belonging to Shell Tanker (U.K.) Ltd., was fitted with calibrated pumping equipment to introduce oil at a known rate on the suction side of the stripping pumps which operated at approximately 100 ton/hour. Tests were carried out some five miles off shore. Two motor fishing vessels and two vessels from the Milford Haven Conservancy Board were used to carry observers, representatives of the oil companies, etc. Three slicks were laid, each one mile in length; these consisted of Kuwait Crude tank slops, Kirkup Crude tank slops and heavy fuel oil (6,000 sec^{-1} Redwood I at 100°F) tank slops. The slicks were laid parallel, one after the other, and an observer boat was carefully positioned in the center of each slick. Each slick behaved in a similar manner; it was clearly visible on first being laid, but soon became wider, thinner and less clearly visible. Small blobs of oil were seen at times in all three slicks. The slicks were all lost after three hours, observation and a spotter aircraft which was used reported no trace of the oil slicks; they were assessed as having disappeared after about 4 hours. The fourth control boat made a careful traverse of the whole area without observing slicks, or oil blobs. It was therefore concluded that a discharge of oil slops at a rate not exceeding 2 feet^3 oil/mile traversed would not appear to produce harmful pollution in the open sea. As a result of these trials, the U.K. proposed amendments to the Oil Pollution Convention.

Oil Water Separators

As a result of its work with IMCO, the Warren Spring Laboratory became interested in the problem of testing oil water separators intended for shipboard use and also in their design. One of the Laboratory staff had some years earlier carried out experiments on the separation of oil from water and had obtained a patent on a particular type of filter unit. This officer resumed his experiments and finally invented an alternative type of oil water separator, or coagulator, which showed considerable promise. This invention was then the subject of a good deal of development work by the Laboratory and now an oil water separator, the subject of various patents, has been developed.

Conclusions

This paper has discussed the work of a number of laboratories over a period of nearly 10 years. A good deal of other work in other departments and in private firms has gone on at the same time, in particular no reference has been made to the work of the Ministry of Defence (Navy) on the movement and fate of floating oil. In all of this work, from the very beginning, there has been the closest collaboration between Government laboratories and the laboratories of the major oil companies in the United Kingdom; without this collaboration much of the work would have been impossible.

In conclusion, the author would like to thank his many colleagues in the various laboratories of the Ministry of Technology, who have made their material available and in many cases have supplied hitherto unpublished documents for this purpose.

Research And Engineering Are Mandatory To Reduce The Risk Of Oil Spills

Honorable Russell E. Train
Under Secretary
Department of the Interior

(Monday Luncheon Speaker)

Fifty years ago the dream of every wildcatter in Oklahoma, Texas, or California was to drill in a gusher. The picture of oil, drilling tools, wire cable, and pipe blowing out over the derrick top several hundred feet in the air and raining over the countryside, oil overflowing the slush pit and running down the creeks was a picture of success. In fact, the word "gusher" is a fixture in our vocabulary and is defined in Webster as an oil well with a copious natural flow. In the early days of the industry, there were some very spectacular gushers.

A particularly wild one was the Lakeview gusher of the Midway-Sunset field of California. On March 14, 1910, this well "blew in" producing about 18,000 barrels of oil the first day. Within a few days, the well was far beyond control. Oil continued to flow to the surface for 18 months and finally was stopped on September 9, 1911, after it had produced over 8 million barrels of oil. Three years later, an adjacent well got out of control and gushed about 6 million barrels and formed a 60-foot wide crater where the well head had been.

There is no doubt that the wildcatters regretted the loss of the oil and the payments for land damage to the farmers. But the drilling technology of the time was not developed to the extent that flowing wells, particularly the larger ones, could be controlled.

The situation now is greatly changed. The ounce of prevention through use of modern drilling technology with the use of drilling muds, gas chromatograph monitors, and blowout prevention equipment has been developed to contain the tremendous energy of a highly charged oil and gas reservoir, and has all but eliminated the highly spectacular, but highly uneconomic and polluting gusher.

Just how far technology has advanced was dramatically shown during Hurricane Camille last August. This was a 100-year frequency storm with wind gusts up to 210 miles per hour and 20-foot tides. Over 100 million dollars of damage was done. Within the offshore oil fields, two platforms along with their rigs were toppled. In addition, 4 other rigs were partially or wholly blown off platforms. In spite of this severe damage, a check of the area by the U.S. Geological Survey revealed no oil slicks in Federal waters and only minor ones in State waters. Petroleum companies, by applying safety measures, prevented major pollution. They should be proud of this record, and I commend them on it.

At the same time, problems of control of oil spills still exist. The distressing event at Santa Barbara clearly shows that the technology of prevention and control of oil spills is not sufficient to meet all situations.

This is not so much because the technology is not constantly improving, as it indeed is, but because the problems of exploration, production and transportation are becoming increasingly complex. In such cases, the proper ounce for prevention is not always obvious. The progression by the oil industry from land to the offshore introduced a completely new set of problems. Wave damage during storms, the corrosive effect of sea water on metal, the navigation hazards of stable platforms, unstable sea bottom foundation conditions, and the general difficulty of working under water are only a few of the new problems that had to be met. As industry moves still farther into deeper water, more hostile seas, and more remote areas, these problems will increase in complexity.

There is no escape from this direction of development. As older petroleum provinces of the country pass their peaks of production and the demands for energy increase, there is no choice but to go to the more remote and more difficult areas for the petroleum supplies to meet the demands of our geometrically increasing society—a society, whose very existence is threatened by its own enterprise.

The risk of oil spillage increases in direct proportion to three factors—the amount of oil handled, the time of the handling, and the difficulties of handling. All three are increasing rapidly. First, we are handling greatly increased amounts of oil and gas. 2.8 billion barrels of oil were consumed in 1966. By 1980, it is forecast that consumption will exceed 4 billion barrels. This means more pipelines, more tanker dockings, and new port facilities. We are handling this increased amount of petroleum for longer periods of time as the required transport distance between the oil field and the market increases. Finally, we are having to produce and transport oil where more natural hazards are present and the difficulty of handling increases. Hazards, such as deep and stormy waters, sea ice pressure ridges and icebergs, permafrost, earthquakes, and tectonic activity must, by necessity, be considered in the systems designed to reduce the risk from accidental oil spills.

The most striking example where all three factors come clearly into focus is on the North Slope of Alaska. It is apparent that this area may ultimately rank as one of the major petroleum provinces of the world, hopefully rivalling the Middle East in productivity as well as reserves. There is no question but that the United States must turn to this province to help satisfy its greater demands for oil. The distance from well head to market is great, 5,000 miles to the East Coast and 2,500 miles to the West Coast of the United States. The natural hazards of production and transportation are more formidable than for any other region on earth. On the North Slope itself, wells must be drilled and produced through about 1,000 feet of permafrost, much of which turns into a fluid mud when thawed. The problems of drilling in permafrost have been difficult, and there is little question that the problems of production will be more demanding.

Transportation of oil from the Arctic reservoirs presents great problems. Laying and maintaining a pipeline carrying hot oil through the permafrost areas will be a very expensive engineering project. Because of the permafrost, the pipeline faces formidable engineering problems not yet solved. A pipeline to the south must pass over the rugged Brooks Range, and the more rugged Alaska Range. The Alaska Range and the region southward to Valdez are noted for their tectonic activity and resultant earthquakes, avalanches, and landslides. If you will recall the Alaska Earthquake of 1964, you can perhaps get some measure of this type of hazard. Going the ocean route to the East Coast, giant tankers must make the voyage through the Northwest Passage from Prudhoe Bay through thick sea ice and pressure ridges and around icebergs under adverse weather conditions.

The production and transportation of oil from the North Slope of Alaska are problems we face now, but we can foresee perhaps even more formidable problems a few years away, when exploration and possibly production turns to areas such as the stormy seas of the Gulf of Alaska and the ice-clogged Beaufort Sea shelf. These hostile seas are not adequately explored, but may contain petroleum provinces that rival the North Slope.

The prevention and control of oil spills call loudly for parallel courses of action. We must first of all evaluate and take steps to lower the risks of spills, we must determine what level of risk is acceptable to our society, and we must prepare to take corrective measures when accidents occur.

I mentioned earlier that the factors that increase the risk of oil spills are themselves increasing. The factor that reduces the risk is technologic advance based on research. Research of many different kinds is needed—research on the geologic setting of newly discovered oil fields and projected pipeline routes to evaluate the geologic hazards; engineering research on drilling, production and transportation of petroleum; and research on control and clean-up of oil spills. With this new knowledge, we can evaluate the risks encountered in new areas and constantly lower these risks.

In order to determine the level of risk acceptable to our society, again additional research must be undertaken. We must know what the short and long term harmful effects of oil spills really are. There must be open public discussion solidly based on knowledge and alternative courses of action. Only thus, can we approach rationally the problem of regulatory control.

We must have engineering practices and integrated codes of regulations that are strong enough to control, realistic enough not to stifle, and flexible enough to meet changing conditons. This seems particularly important to industry for reaching the difficult management decisions that must be resolved on the basis of economic considerations.

The factors that increase the risks of oil spills are getting worse at a time when man is slowly awakening to the chilling fact that he can, through industrialization and over-population, irreversibly degrade his environment to the point that he may have to engage in a major effort to survive as a species. It is ironic that man's dream has been to apply science and technology to overcome problems on earth, to eliminate famine and pestilence, and to upgrade his standard of living.

Nathaniel Owings observed in his recent book, *The American Aesthetic*, "... Man's activities have reached the point where nature and civilization have influenced each other so completely as to have established one system, one ecology, one total environment from which come the conditions that govern our lives."

Man, at least in our western society, has considered himself the most important element on this planet. To accommodate himself, he has modified his environment as he felt necessary—and, too often, with complete disregard for the future. I consider it unlikely, at least in the short run, that the ethical basis of man's action is likely to change. It is useless to question whether man should or should not modify his environment—he will because he cannot avoid doing so. The problem, and our objective, must be to assure that the results of his actions are foreseen and are compatible with preserving a balanced ecosystem in which mankind can be sustained on earth. Our goal must be to develop a dynamic society in harmony with its environment.

The people of the United States are insisting on a reordering of national priorities and we ignore or miscalculate the significance of this movement at our peril. I predict that quality of the environment will become the major issue of our time and will require our institutions—both public and private—to reorient our planning, our goals, and our budgets.

For many decades the people of the United States have held as their major national objective a continuing improvement of the American standard of living. Coupled with great personal freedom within a free enterprise system, we have amassed immense national wealth and a phenomenal standard of living in comparison to other nations. Our industrial society, fueled by the energy provided by a strong basic resources industry, is now a mature one; but it requires ever more materials from the earth to satisfy its voracious appetite. What lies ahead?

I submit that the GNP must no longer be the sole measure of our nation's success. We need a new measure—one that is directed to quality rather than mere quantity. If we insist that our standard of living must be sustained and not imperiled, our obligation increases to direct more attention, planning, and expenditure to protect and to fortify our landscape, our water supply, our atmosphere, our waterways, our open spaces—indeed, our *total* environment. To the parameters of geologic potential, engineering technology and traditional economics, which served industry in our formative years, must now be added a fourth parameter—the quality of our environment.

We in government are re-examining our own priorities and our own organizations in order to meet more effectively the growing insistence of the American people for quality of life—indeed, so that we are enabled not just to respond but to give positive leadership to rising public aspirations for a decent world in which to live.

How will industry rise to this challenge? In particular, how will you of the energy industry respond? On your answer here today, in your board rooms, and in your business decisions in the months ahead—rests much of the future of our people.

PREVENTION AND CONTAINMENT OF OIL SPILLS

Monday, December 15, 2:00 p.m.

Chairman: RAdm. R.W. Goehring
Chief, Office of Operations, U.S. Coast Guard

Co-Chairman: C.G. Cortelyou
Coordinator, Air and Water Conservation
Mobil Oil Corporation

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Prevention Of Pollution By Oil And Hazardous Materials In Marine Operations

Commander Albert G. Stirling
Chief of Electrical Engineering Branch
U.S. Coast Guard

Abstract

A brief summary of legislation and international treaties applicable to pollution by marine operations is given. Pollution is defined as the discharge of anything which affects or is harmful to the ecology, use, or esthetic quality of the receiving body either temporarily or permanently. The causes of pollution are deliberate violations, poor practices, and unavoidable accidents. The solution to pollution is prevention, minimizing effects when total prevention is not realistic, and finally cleanup. These solutions are best effected by education, engineering, and enforcement, in that order. Data is presented which points out the major operational causes of pollution with the not too surprising result that human error, manifested in overfilling, vessel mishandling, and improper system operation, is the major contributor. Possible corrective measures are discussed with emphasis that all such measures must meet the test of necessity, effectiveness, and practicality.

Introduction

The basic reason to prevent pollution is to protect our natural resources. This justification has, of course, always existed, but it has only been the recent public enlightenment on this subject which has given it the necessary importance. Prior to 1956 there was little public support for pollution control, and legislation was limited to: The Refuse Act of 1899, The Oil Pollution Act of 1924, and the Tanker Act. However, the growing public concern about our water resources is amply reflected in the legislation since 1956.

1956	Federal Water Pollution Control Act
1961	Amendments to the basic Act
1966	Clean Water Restoration Act
1969	Water Quality Improvement Act (HR 4148).

If the basic need and public opinion have failed to instill the desire for pollution control upon industry, the liability provisions of the 1969 Act; if enacted, surely will. This liability makes pollution control an economic fact of life for industry.

A similar trend in anti-pollution exists on the international scene. The first real effort was the International Convention for the Prevention of Pollution of the Seas by Oil 1954. This convention was amended in 1962 and the amendments were incorporated into Subchapter 0, Title 33, Code of Federal Regulation in October of 1967. Just this past September the Maritime Safety Committee (MSC) of the Intergovernmental Maritime Consultative Organization (IMCO) approved additional amendments to the Convention. When these amendments are ratified by a sufficient number of countries, they will have the far-reaching effect in essentially prohibiting all discharges. Detailed operational specifications for oily-water separators and oil detectors are also being developed by the Maritime Safety Committee.

The problems and possible solutions discussed in this paper are directed at marine vehicles and not off-shore drilling or production vessels or platforms. There is no intent to slight the problem as it relates to these latter structures. The limited time available for this paper does not permit an adequate coverage of the subject. The problems of off-shore storage facilities, pipelines, and the newly popular submerged storage tanks present their own unique and difficult problems.

Problem Definition

What is Pollution? Basically pollution is the discharge of anything which affects or is harmful to the ecology, use, or esthetic qualities of the receiving body. Pollution may take the form of heat, trash, oil or other material or energy forms. The pollution may be either permanent or temporary.

The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

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TABLE 1. CAUSES OF POLLUTION

	1968		1967		1966		Total	
	Number	%	Number	%	Number	%	Number	%
Overfilling	67	9.5	9.6	26.55	53	8.4	176	33.7
Holed	38	5.2	34(26)*	16.1	23	8.0	95	18.2
Bilges	32	4.5	27	12.8	41	14.2	100	19.2
Leaks	27	3.8	30	14.2	28	9.8	85	16.2
Pumped	16	2.3	32	15.2	18	6.3	66	12.7
Other	283(181)*	39.7	13	6.2	12	4.2	309	–
Unknown	250	35.0	19	9.0	112	39.1	381	–
	714	100.0	211	100.01	287	100.0	1212	100.0

*Barges

The latest IMCO proposals to the 1954 Oil Pollution Convention have eliminated the concept of prohibited and non-restricted discharge areas and treats all waters the same. IMCO seeks to end the dilution solution to pollution by limiting the discharge from other than tankships to less than 100 parts per million (ppm) and less than 60 litres per mile. The criteria for other than bilge discharges from tankships is similar except that the total quantity discharged is limited to 1/15,000 of the total cargo capacity in lieu of the 100 ppm and such discharge is restricted to more than 50 miles offshore. Essentially then, we are looking to the prevention of the discharge of oil in any quantity.

Although each hazardous material or groups of hazardous materials must be individually considered, it should be readily apparent by their very designation that a similar prohibition of discharge is necessary.

The causes of pollution. The basic causes of pollution are considered to be poor practices, accidents, and deliberate violations. The means to rectify these causes are education, engineering and when all else fails, enforcement. Poor practice, of course, is the area most amenable to correction and wherein education and engineering are most effective. Under the heading of "poor practice" are such things as systems, equipment, procedures, personnel training, and maintenance. Is the system provided the best and least likely to cause problems? Is the system being operated in the optimum manner? Do the people know what they are doing? And finally, is the equipment properly maintained? Education and engineering can provide affirmative answers to these questions.

Despite our best efforts, accidents will occur. People will make mistakes and equipment will fail. Here education and knowledge have failed us, and we must rely on engineering to minimize the opportunity for accidents and their effects.

Of course, the only solution to the deliberate discharge of pollutants is the brute force of strict enforcement. Here again, education has failed, and although engineering can make deliberate discharges difficult or offer an alternative disposal method, only the positive assurance that one won't get away with it will eliminate this deliberate pollution.

Pollution Data. The following data from pollution reports collected or submitted to the Coast Guard gives some feel for the causes of pollution. This date is for calendar years 1966, 1967, and 1968. The increase in reported pollution incidents in 1968 is more a reflection on our reporting procedures and increased emphasis on the problem rather than an increase in pollution incidents. The information to be gleaned from this data is the generally consistent relative standing of the causes of pollution in each year.

The data is generally self-explanatory with the possible exception of the term "other". This includes items reported as equipment failure, personnel error, or were related to shore facilities such as settling ponds overflowing.

The 1968 data shown in Table 1 was also broken down by general location of the spill:

Piers	382	Coastal	15
Harbors	212	Oceans	8
Inland	97		

The complete report from which this data was extracted is attached as an appendix to this paper so that each reader may make his own appraisal of the limitations on the data.

Of the 714 reported spills in 1968 only 21 were estimated to exceed 100 barrels of material.

Data Analysis. The obvious and not too surprising conclusion which this data shows is that human error is the principal villain in pollution. It further appears that the majority of these errors are in relation to the handling or preparation for handling of liquid cargoes. It should be

TABLE 2. SOURCES OF POLLUTION

	1968	1967	1966	Total
Tankers	84	82	56	222
Dry Cargo	112	67	64	243
Barges	68	64	57	189
Military	50	52	70	172
Pass	3	4	4	11
Misc.	29	7	17	53
Unknown	2	1	19	22
	248	277	287	912

apparent that education (training) and engineering can be very effective in pollution prevention.

Possible Solutions (Prevention)

As indicated earlier, the prevention of pollution has two aspects. The first is total prevention and the second, knowing full well that nothing is perfect, is minimizing or containing the pollution incident. This section is essentially the prevention aspects with possible minimizing actions to be discussed in the following section.

A few words appear in order to amplify the intent of the remainder of this paper. It is *not* the intent to give pat solutions. It is *not* the intent to advocate changes to the status quo in each and every area mentioned. It is intended to mention areas where improvements may be possible and where the cost-benefit ratio of such improvements should be carefully considered.

It must be recognized at the outset that pollution [illegible] prevented if society is willing to pay the price. Thus one solution is to prohibit the carriage of pollutant commodities. This, of couse, is unreasonable. Therefore, compromise or the cost-benefit of the solution must be considered. There is a great deal which can and will be accomplished at negligible costs. Other necessary solutions will be reflected in product costs. The critical problem is, of course, in deciding at what point the price is too high. Every solution must answer to: Is there a need? Is it effective? Is it practical?

As indicated above and amplified in the appeandix, the existing data on sources of pollution is limited and suitable for only very general conclusions. Possibly one of the major contributions of HR 4148 will be the requirement to report spills. The mandatory reporting of spills will permit a meaningful system of data collection and analysis of pollution sources and causes. This will provide not only an indication of problem areas, but will reflect the effectiveness of the solutions imposed. Only by such a continual evaluation of the problem can an effective pollution prevention program be realized.

Terminal Facilities. The question may be asked that if this paper is limited to marine operations, why should terminal facilities be discussed, and how far ashore does one go in defining marine operations? The previously given data provides us with a logical answer and demarcation of responsibilities. Since a great deal of pollution results from loading/unloading operations, one must be concerned with the control and containment of the product in that system which is involved in loading/unloading the vessel. Therefore, an end point for consideration should be the shore receiving or storing tank shutoff valve.

Personnel. Probably not only the greatest opportunity to improve pollution prevention but also the most cost effective means is better trained and more concerned personnel conducting the product handling. Improvement must not be limited to personnel capabilities. Stress must be given to personnel attitudes, a sense of responsibility, and a real desire to eliminate product spills. Subpart 46 CFR 35.35 of the U. S. Coast Guard's rules and regulations requires licensed or certificated personnel to be in charge of the vessel and delineates their responsibilities. Consideration should be given to a similar licensing/certification program for the man-in-charge of the shoreside operations and for a better definition of the authority and responsibility of such personnel.

Hand in hand with this delegation of authority and responsibility, would be an expanded version of the "Declaration of Inspection" required by the Tank Vessel Regulations, 46 CFR 35.35-20. This Declaration would be expanded to cover pollution prevention related factors and also to be applicable to the shoreside facilities.

Equipment. The present systems for loading tank vessels must be re-evaluated with product containment and anti-pollution factors given more emphasis. The use of flexible non-metallic hose is an obvious candidate for consideration. If non-metallic hose is permitted, should it have a specified useful life with periodic pressure tests and inspections? This is obviously an area where better data would permit a definite conclusion.

The present systems should also be examined and possibly re-engineered to reduce the opportunities for human error. Do the systems really need the multitude of valves and possible inter-connections, which are frequently incorrectly set up? Has the system some capability of emergency response such as remote controlled shutoff valves? Do the systems provide adequate information to the operator as to product, quantities, velocities, temperatures and pressures? Ship design is toward a console controlled remote operated system. The shore facilities should equal or exceed the vessel capabilities.

Procedures. Intimately related to equipment design, selection and personnel training, is the proper use of the equipment. Many people will offer equally many different ways to do a job, but only one may be correct for the particular system in use. As examples, should one tank be loaded quickly or three tanks slowly? To clean the pipelines, should one blow back or take suction? Each system must be examined for its best operation regardless of its intended design characteristics and the operating personnel then trained in this procedure of operation. The operational procedures are too often taken for granted. After all, "everybody knows that".

Maintenance, inspection and testing. This subject speaks for itself. Everyone can recite the advantages of such programs and can mention numerous spills which shouldn't have happened. The State of Connecticut in its Public Act No.765 is considering licensing all chemical or petroleum terminals and, as part of such licensing, will require a maintenance program.

Slops, Drains and Returns. Terminals must provide reception facilities for the residual slops on board the vessel and for product drain and return lines. Since overfilling is an apparent common cause of spills, possible solution is an overflow return to the terminal with tank overpressure protection.

Vessel Facilities. The evaluation of the vessel for the prevention of pollution is more difficult than a terminal facility since the vessel is subject to varying conditions. Pollution from a vessel may occur during cargo handling operations or as a result of a low or high energy impact. A low energy impact is defined as a collision or grounding whereby the vessel is easily repaired or refloated. A high-energy impact would be *Torrey Canyon* or *Ocean Eagle* wherein the vessel is lost or salvaged in such condition as to require major reconstruction.

The Subcommittee on Ship Design and Equipment of the Maritime Safety Committee (MSC) of the Intergovernmental Maritime Consultative Organization (IMCO) has been, since the *Torrey Canyon* incident, considering various ship factors which effect pollution. It has basically been the United States' position at these meetings that any reduction in the probability of occurrence or seriousness of a high energy impact accident will come from ship control and operations essentially independent of ship design. Therefore, in the following discussion, product handling and low energy impact incidents will be considered first and separately from the high energy impact incident.

Personnel. Ship board personnel are presently required to be licensed and/or certificated by the Coast Guard. The regulations, 46 CFR 35.01-40, stipulate that vessels shall be operated as to prevent the discharge of oil in accordance with our treaty commitments. However, the training requirements and specified duties are, at present, not fully pollution prevention oriented. The necessary additional emphasis in the regulations concerning pollution prevention will be initiated by the Coast Guard. However, the necessary additional training must be provided by industry and the various seamen's schools.

The existing Coast Guard licensing/certificating program is directed toward safety with pollution prevention being only a by-product. A Merchant Mariner's license is renewable every five years and a tankerman's certificate is valid until revoked. Since human error appears to be the predominant factor in pollution, perhaps a mandatory retraining program should be prerequisite to license/certificate renewal at specified periods.

Tanks. To date it appears that cargo tanks have been of adequate strength. It does appear that tank size, location, and corrosion resistance are subjects for re-evaluation.

Tank size has grown as have vessels, until today, many single tanks nearly equal the capacity of older vessels. Tank size must be evaluated for optimum size considering cargo handling, gas freeing, susceptibility to rupture caused by grounding or collision, and quantity of product which would be released.

Tank location or protection from damage by isolation has been discussed for some time. The continued use of single side skin construction for barges and ships is seriously questioned. The question of double bottoms is not so clear. Vessel bottoms are somewhat less susceptible to rupture damage and leakage from a bottom failure is limited by the external hydrostatic pressures.

The elimination of skin tanks will provide the added benefit of available tankage for clean ballast, thus eliminating an additional source of pollution.

Tank Venting, Sounding, and Overflows. On most existing vessels when overfilling occurs, there is no alternative to a spill. Since overfilling is a principal source of pollution and since overfilling will never be fully eliminated, the tank system should be designed to accommodate a short term overfilling condition. Two alternatives are a system of overflow lines to an overflow tank or a shore return for the excess product. Such a system is well within the technological and economic limits of pollution prevention.

Cargo Piping and Control Systems. Shipboard cargo piping systems appear to be structurally adequate. However, in many cases their complexity enhances the opportunity for human error.

The cargo manifold area is a continual source of spills during the transfer operations. Present procedure is to provide drip pans, sand, and scrupper plugs. Why not place all manifold connections or other such high spill prone areas in wells with a shore return? Such an arrangement would handle a rather large leak without product loss to the environment.

The trend to the cargo control room concept provides more accurate and continuous cargo status indications and vastly increases the response capability of the personnel. A well designed control system will also reduce the opportunity for human error. A desirable feature which can be easily provided in such a system is remote emergency cargo system shutdowns located at strategic positions about the vessel.

Oily Water Separators and Oil Detectors. The development of oily water separators and oil detectors has received a great deal of international attention since the *Torrey Canyon*. Annex II of IMCO document OPVII/WP. 4 dated 11 September 1969 is a proposed specification and test standard for these devices. To the author's knowledge there does not exist any equipment which will without qualification meet these standards. The detection of oil in water at less than 100 parts per million at any reasonable flow rate is difficult. Likewise, the separation of oil from water to better than these proportions for all conditions has resisted development to date. Furthermore, discharge of this quality effluent is limited to the nonprohibited areas. Strictly speaking, for use in coastal waters, the devices must detect or provide an oil free discharge. This author is not optimistic in the development of such equipment and, therefore, recommends design and development efforts in other directions to circumvent the need for such devices.

Vessel Design and Manuevering Characteristics. Considering the basic vessel design and machinery, there appears to be little need for basic change except for improvements in manuevering and handling characteristics, particularly during docking. Here again, data is lacking to pinpoint the precise causes of the holed vessels; however, elimination of single skin vessels may make pollution from this source relatively insignificant.

Vessel Protection (High Impact). The IMCO committees have been studying the problems of anti-pollution as a result of high impact since the *Torrey Canyon* incident. The entire gamut of ship design and equipment from emergency power for steering to side blisters has been brought up. Although one can support design modifications based on hypothetical situations, an analysis of high impact type incidents shows human error and poor judgment to be the basic faults.

The best solution to high impact collisions or groundings appears to be in the area of more precise navigation systems, restricted routing, sea lanes, traffic control, and more prudent seamen.

The structure of power requirements necessary to resist the momentum and impact energy of today's vessels is just not practical.

Possible Solutions (Minimizing).

Knowing that vessels will be in collision and will be run aground, what design features will help minimize the possible effects? Structurally, tank size and isolation could reduce the amount of pollutant released. Additionally, provisions can be made to remove or otherwise contain the cargo.

A not overly expensive nor unreasonable requirement would be to provide connections for external power to the ships pumps and cargo system. This would permit the use of the installed equipment to remove the cargo to another vessel or container. A corollary to this would be the provision of connections to the ships tanks via the installed piping systems to permit external pumps to remove the cargo.

An additional provision is some form of emergency containment. This could be in many possible forms. One for limited damage cases is to transfer the cargo into normally empty or clean ballast tanks. A second means would be to carry onboard inflatable containers such as envisioned in the Coast Guard's air transportable recovery system. A "way out" solution might be the use of jelling or hardening agents.

Summary

The problem of pollution-free marine operation possesses no insurmountable obstacles or requires no technological breakthorughs. Solutions and technologies are known which will stand the test of: Is it necessary? Is it effective? Is it practical? What is presently lacking is the incentive for accomplishment. If public opinion and the needs of mankind are not sufficient, then strict enforcement under the new legislation will be necessary. However, to plagiarize from Smokey the Bear: "Only *you* can prevent pollution".

APPENDIX

STATISTICS ON WATER POLLUTION VIOLATIONS REPORTED BY THE U.S. COAST GUARD IN 1968*

Completeness and Accuracy of the Data

These statistics were obtained by tabulating the reports of 1968 violations of federal water pollution laws received by the Law Enforcement Division, U. S. Coast Guard Headquarters, from Coast Guard field units. These reports were made on Coast Guard form CG-3639 and are kept on file, along with reports of the two previous years, in the above office. Supplementary descriptive material and statements by investigating officers, witnesses, and operating personnel were attached to form CG-3639 in about a third of the reports.

Only those cases of pollution which are considered possible violations of federal law are required to be reported by field units, although a few of the reports describe incidents which were clearly not violations of federal law. An important type of pollution specifically exempted by federal law is any liquid which flows from public sewers.

Federal law is also somewhat vague as to what substances and concentrations are considered illegal. All non-oily industrial wastes which enter U. S. navigable waters, except through public sewers, are open to question in this regard, and in practice field personnel use some discretion in not reporting very minor incidents. Almost all spills of oil or oil products constitute violations, however, and are reported if known to the Coast Guard.

A major problem encountered in extracting data from the reports was the fact that the form CG-3639 was designed primarily to provide information for law enforcement rather than for statistical purposes. The form has no spaces for an estimate of the quantity spilled, the cause of the spill, the methods and effectiveness of cleanup, or other information which would be of value for assessing the gravity and causes of water pollution. When information was not explicitly included on the form or in attached supplementary materials, the tabulator recorded the most probable circumstances whenever he felt at least 80% confident of them. A new pollution violation report form is currently being developed to include more complete information on all aspects of pollution incidents.

Since form CG-3639 does not request an estimate of the quantity of pollutant and since such estimates are usually very difficult to make, only about half of the reports included any indication of the quantity. It is estimated that all but about 30 of the spills were less than 100 barrels. The 21 spills which were reported to exceed 100 barrels are discussed toward the end of this report.

A. General Area	Number of Cases
1. Atlantic coast (including Puerto Rico and Virgin Islands)	226
2. Pacific coast (including Alaska and Hawaii)	340
3. Gulf Coast	93
4. Great Lakes and all other fresh waters	55
Total	714

B. Type of Location	
1. At a dock	382
2. In a harbor but not near a dock	212
3. Other inland waters	97
4. Coastal zone of the sea (within 3-mile limit)	15
5. High seas (beyond 3-mile limit)	8
Total	714

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*Source: Violation Reports Received by the Law Enforcement Division, U.S. Coast Guard Headquarters, Washington, D. C., During Calendar Year 1968

C. Source		Cases
1. Vessels		
a. Tankers		84
b. Dry cargo		112
c. Barges		68
d. Navy		50
e. Passenger		3
f. Miscellaneous (mostly tugs & fishing vessels)		29
g. Unidentified vessels		2
Subtotal, Vessels	348	
2. Onshore sources		
a. Loading terminals		58
b. Other onshore sources		227
Subtotal, Onshore sources	285	
3. Offshore structures		9
4. Unknown sources		72
Total		714

D. Nationality of Vessel Sources

1. U.S.	244
2. Foreign	102
3. Unknown	2
Total	348

E. Pollutant

1. Persistent heavy oil	480
2. Transient light oil	51
3. Other (see notes)	183
Total	714

F. Cause

1. Personnel failure		
a. Overfilling		67
b. pumping bilges		32
c. other willful-dumping by vessels		16
d. pumped overboard-during salvage		1
e. other (see notes)		180
Subtotal, Personnel failures	296	
2. Equipment failure		
a. ship-to-shore		19
b. shipboard piping		6
c. shipboard pump		2
d. collision with other vessel		2
e. grounding		8
f. other hull ruptures		28
g. other (see notes)		103
Subtotal, Equipment failures	168	
3. Cause unknown		250
Total		714

G. Cleanup Resources (when specified in reports)

1. CG OSC only	41
2. CG OSC and resources	12
3. Non-CG federal (mostly Navy for Navy spills)	77
4. Private resources	119
5. Local government cleanup	11
Total	260

H. Sources of Notification	Cases
1. Reported by CG patrol	72
2. Reported by spiller	92
3. Reported by Navy (almost all were Navy spills)	81
4. Reported by other federal agency	4
5. Reported by private citizen or local official	124
6. Source of notification not specified or not tabulated	341
Total	714

I. Methods of Cleanup (when mentioned on Violation reports)

1. Booms	55
2. Chemical emulsifiers	147
3. "Skimmers"	12
4. Straw	3
5. Sawdust	2
6. Vacuuming (usually by a truck)	12
7. Fire hose for dispersion or containment	4
Total	215

J. Cases in Which Samples of Pollutant were Taken

1. Samples taken (usually 2 or 3 in each case)	453
2. No samples taken	261
Total	714

K. Cases in Which Signed Statements were Obtained

1. From civilian witnesses not involved	177
2. From civilian operating personnel	126
Total	303

Specific Notes on the Data

B-3. "Other inland waters" includes all fresh waters plus coastal bays and sounds.

B-5. Many spills on the high seas undoubtedly go undetected.

C-2. "Other onshore sources" are mostly industrial plans disposing of chemical wastes, ruptured fuel tanks and pipelines, and vehicles.

E-2. "Transient light oil" includes light diesel oil, kerosene, and gasoline.

E-3. "Other pollutant includes a large number of chemical wastes identified only by pH valves, as well as various chemicals like xylene, toluene, and benzene, various kinds of solid materials like trash, asphalt, and lumber, and unidentified pollutants.

F-1. "Other" personnel failures include improperly opening or closing valves on ships and shore and many other types of personnel failure that were very difficult to classify more specifically, as well as causes reported only as "personnel failure" without more specific information.

F-1. and **F-2.** Because of close interaction between personnel and equipment, it was often difficult and somewhat arbitrary to identify a cause as either "personnel failure" or "equipment failure". Failure of equipment was often the result of faulty operation or maintenance, and equipment was sometimes inadequate to perform the intended function. These cases were generally counted as personnel failure. A number of cases resulted from chemical settling ponds overflowing because of unusually heavy rainfall and were counted as equipment failure.

F-2. "Other" equipment failure includes valve failures, miscellaneous shipboard equipment failures, all equipment failures not occurring aboard ships, and causes reported only as "equipment failure" without more specific information. At least 8 pipeline breaks on shore, 3 submarine pipeline accidents, and 2 unspecified pipeline accidents, plus 2 underground fuel tanks leaks are included.

F-3. "Cause unknown" signifies either that the cause was unknown to the reporting unit or that it was known to the reporting unit but was not included in the report. The pollution report form does not have a space for indicating the cause of the spill, other than provision for checking "personnel failure" or "equipment failure", and the specific cause could be determined only when it was mentioned in the remarks section of the form or in attached narrative summaries and statements.

I. "Methods of Cleanup". This data indicates the number of reports in which each type of cleanup method was mentioned as used. Often more than one method was used for a single spill. This data is incomplete since the report form does not call for information about cleanup other than asking what action was taken to eliminate any fire hazard.

J. and K. Note that the figures represent the number of cases, not the number of samples or statements. K-1 and K-2 cannot be meaningfully added since both types of statement were often obtained on a single case.

Spills Over 100 Barrels

Twenty-one spills were reported as being over 100 barrels. Of the large number of reports (about half of them) in which the size of the spill was not indicated, probably about 10 exceeded 100 barrels. The following data applies to the 21 known cases:

Median size: 275 barrels.

Largest spill: 70,000 barrels (OCEAN EAGLE).

Pollutant: 16 persistent heavy oil, 3 transient light oil, 1 xylene, and 1 spent sulfuric acid.

Source: 6 barges, 3 tankers, 1 passenger ship, 1 miscellaneous craft, 4 loading terminals, 1 oil truck accident on shore, 2 ruptured pipelines onshore, 2 other onshore sources, and 1 offshore structure.

Area: 9 on Atlantic coast, 7 on Pacific coast, 4 on Gulf coast, and 1 on a river.

Location: 9 at dock, 8 in harbor, 2 on other inland waters, 1 in coastal zone of the sea, and 1 on high seas.

Causes: 3 hose ruptures, 2 ruptured shore pipelines, 1 shipboard piping failure, 3 groundings, 1 collision between vessels, 2 cases of overfilling, 1 oil truck accident onshore (oil flowed through city sewer), 4 other personnel failures, 1 other equipment failure, 2 cases involving both equipment and personnel failures, 1 unknown cause.

Cleanup: CG OSC only in 3 cases, CG OSC and resources in 3 cases, other federal assistance in 3 cases (one of these was spilled and cleaned up by the Navy.), no federal help in 13 cases, cleanup by responsible party in 11 cases.

Method of cleanup (no. of cases): 9 booms, 12 chemical dispersants, 1 fire hose for dispersion, 1 carbonized sand, 1 straw, 3 vacuum trucks, 1 skimmer, 1 absorbent granules for physical removal.

Prosecution: California Department of Fish & Game intended to prosecute the 3 violations in CGD12.

Comments on Unusual Conditions and Procedures in Certain CG Districts

CGD 1. Many of the 27 violations by shore facilities were fish and poultry processing factories dumping animal remains. (One fish processor commented that he didn't know fish were pollution.) All reports were forwarded to the New England Corps of Engineer District Office. East Coast Services Co. was commonly hired for cleanup.

CGD 3. About 90% of the reports were from COTP New York; these were mostly chemical companies polluting rivers in the harbor with non-oily wastes. Of the 143 cases in this district, 127 were attributed to shore sources, and 101 were non-oily pollutants.

CGD 11. Of the 110 cases 45 were oil spills by Navy ships and facilities. In most cases the Navy hired a commercial firm for cleanup with chemical dispersants, and no Coast Guard investigation was conducted. Eight other reports stated that the responsible party had been cited by California authorities and recommended no federal prosecution.

CGD 12. Of 155 cases 36 were oil spills by Navy vessels and facilities and were usually cleaned up commercially with chemical dispersants at Navy expense. No Coast Guard investigation of these cases was conducted. Twenty-one other reports indicated that the California Department of Fish and Game intended to prosecute, and one stated that the violator had been fined by that agency. These reports usually recommended no federal prosecution. Another 40 reports stated that the California Department of Fish and Game did not intend to prosecute.

CGD 13. Many reports indicated that copies of the report and samples were forwarded to the FWPCA even though no violation of the Oil Pollution Act of 1924 was indicated. Twenty-three of the 36 incidents caused by vessels were from foreign dry cargo vessels; 16 of the 36 incidents resulted from pumping bilges.

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Fluid Dynamics Of Floating Oil Containment By Mechanical Barriers In The Presence Of Water Currents

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Abstract

Experiments on oil containment by mechanical barriers have led to identification of the important physical phenomena controlling the extent of an oil slick and have illustrated flow conditions leading to failure of the barrier.

A mathematical model has been developed to generalize the experimental results. Three regions in the oil layer are identified.

1. *a gravity wave region near the upstream end of the slick, which leads to oil droplet formation if water flows faster than a certain critical speed,*
2. *a boundary layer region where drag of the flowing water causes gradual thickening of the oil, and*
3. *a skirt region where the flowing water causes oil droplets still present to be swept under the barrier.*

Another mechanism of failure is discussed whereby oil could escape under the boom by a kind of draining action.

Example calculations and design charts are presented which may be useful in deciding whether stationary mechanical barriers would work at all in given cases, and in selecting the proper depth of skirt and length of boom required in those cases where mechanical barriers are feasible. Where stationary barriers are not feasible, the results can be used to establish minimum boom drift velocity to prevent oil from escaping.

When oil is spilled on a body of water, it will tend to spread. In order to control such a spill several means are available, one of the most important of which is use of mechanical barriers, or booms. The performance of any boom is affected by wind, waves and currents, but no quantitative information on these effects has been published to permit rational selection or design of booms, or to permit scaling up from model studies to field conditions.

The objective of this work is to present current experimental results and their interpretation on the effects of water currents on oil containment with booms.

Experimental Test Condtions

The tests were conducted in a 6-foot tall by 6-foot wide water channel 60 feet long, as depicted in Figure 1. A 5/8-inch thick phywood board "skirt" was mounted across the tank in the vertical plane perpendicular to the tank walls. Short plywood vortex baffles 6 inches wide were floated at each end of the skirt in order to minimize undesirable end effects due to vortex formation. Water current speed was measured by a calibrated vane-type turbine meter. A glass viewing window in the side of the tank permitted observation of the flow characteristics.

With the current set at about 0.6 feet/sec, oil was poured slowly onto a flat plate just below the water surface to prevent droplet formation and penetration into the flowing water. The length of the slick and some oil thickness measurements were made along the tank centerline after the oil had "piled up" into the skirt. The water flow was slowly increased until oil was observed to escape under the central portion of the skirt.

The ranges covered in the tests are shown in Table 1.

Summary of Experimental Observations

The experimental tests showed that the oil slick exhibits a shape typically indicated by the following sketch for water currents less than about 0.6 ft/sec:

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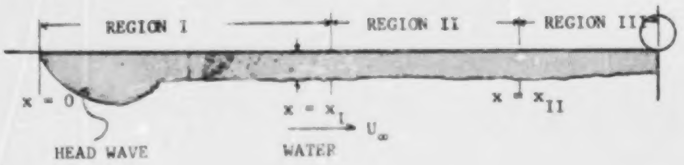

Above about 0.6 ft/sec, more or less periodic traveling waves form in Regions II and III at the oil/water interface. Above about 0.85 ft/sec, oil droplets up to 3/4 inch diameter are torn off the lee side of the head wave in Region I. These droplets are entrained into the flowing water; unless the droplets have sufficient time to rise through the water and rejoin the oil layer before they reach Region III, close to the barrier, they are swept under the barrier. The above observations were found over the range of conditions described in Table 1.

TABLE 1 - RANGES OF THE VARIABLES STUDIED IN THE EXPERIMENTAL WORK

Viscosity	3.7 to 62 centistokes
Specific Gravity	0.864 to 0.914
Volume spilled	10 to 60 gallons
Skirt depth	6 to 12 inches

For all of the experiments the very thick wave at the leading edge of the oil layer was observed. Higher water speeds caused an increasing degree of wave action on its lee side with eventual oil droplet formation, but the general shape shown above remained, even to 1.2 ft/sec, where showers of droplets were torn off.

The Mathematical Model

Objective

In order to relate the experimental observations made within the constrained framework of the tests to other conditions which might be encountered, it is necessary first to identify and understand the natural laws at work which dictate the behavior of an oil slick. Once this is done, mathematical analysis becomes useful to quantify the effects of these laws and to protect their consequences to conditions different from those of the experiments.

Thus, the objective of the mathematical model can be stated simply: to provide for confident scale-up.

Region I

The wave shape formed at the leading edge of the oil layer is similar to the wave shape observed when:

1. A cold front intrudes into warm air[1]
2. Salt water intrudes into fresh water[2]
3. An air cavity flows into a draining horizontal pipe closed on one end[3]
4. Submerged currents of muddy water flow under clearer water[4]

A simple inviscid fluid analysis of this phenomenon, referred to as a gravity wave, was made by Von Karman.[5] He showed that the layer thickness m_I is related to the current speed U_∞ and the densities ρ_o and ρ_w by

$$m_I = \frac{U_\infty^2}{2g_L\left(\frac{\rho_w}{\rho_o} - 1\right)} \tag{1}$$

Experiments by Yih[6,7] verified the predictions of this equation. Von Karman also deduced that the interface at $x = O$ makes an angle of 60° with the horizontal. The predictions of equation (1) are shown in Figure 2 for a wide range of conditions.

Keulegan[2] observed that the head waves in his experiments were about 2.36 times as thick as m_I. Benjamin[8] presents theoretical arguments which show that the head wave must be greater than $2m_I$ in thickness. In the same paper Benjamin shows that the region just downstream of the head wave is inherently unstable.

As Benjamin's theory predicts, our experiments show that the rear of the head wave is unstable. Waves form on the frontal region and grow as they travel to the rear of the head wave. Droplets are torn off the rear of the head wave and are entrained into the water flow. The drop sizes produced were observed to vary up to a maximum of about 3/4-inch diameter. This size is consistent with prediction of the equation

$$d_{max} = \pi \left(\frac{\sigma g_c}{g_L \Delta\rho}\right)^{1/2} \tag{2}$$

developed by Christianson and Hixson[9] from their study of droplet breakup in liquid-liquid systems. Figure 3 shows the predictions of equation (2) for various oil properties. After the droplets were formed, no further breakup was observed. This is consistent with the experimental observations of Rumscheidt and Mason[10] for droplets in a couette flow where the dispersed phase was more than 3.8 times as viscous as the continuous phase.

The velocity at which the oil droplets are torn off the head wave appears to be in agreement with the predictions of a critical value of the Weber number of 22, as suggested by Hinze[11] for gradual acceleration of the dispersed phase.

$$(We)_c \equiv \frac{\rho_w U_c^2 d}{\sigma g_c} = 22 \tag{3}$$

For $\sigma = 30$ dynes/cm and $d_{max} = 0.75$ inch, U_c is predicted to be 0.62 ft/sec. For $d = 1/2\, d_{max}$, U_c is predicted to be 0.88 ft/sec; we have observed visually that oil droplets of 0.4-inch diameter have a high frequency of occurrence at about 0.9 ft/sec. water velocity. Figure 4 shows the predictions of equation (3). The drop size obtained from equation (2), when used in equation (3) gives the critical velocity below which no drops form. Above this velocity

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[1] Superior numbers refer to literature references at conclusion of text.

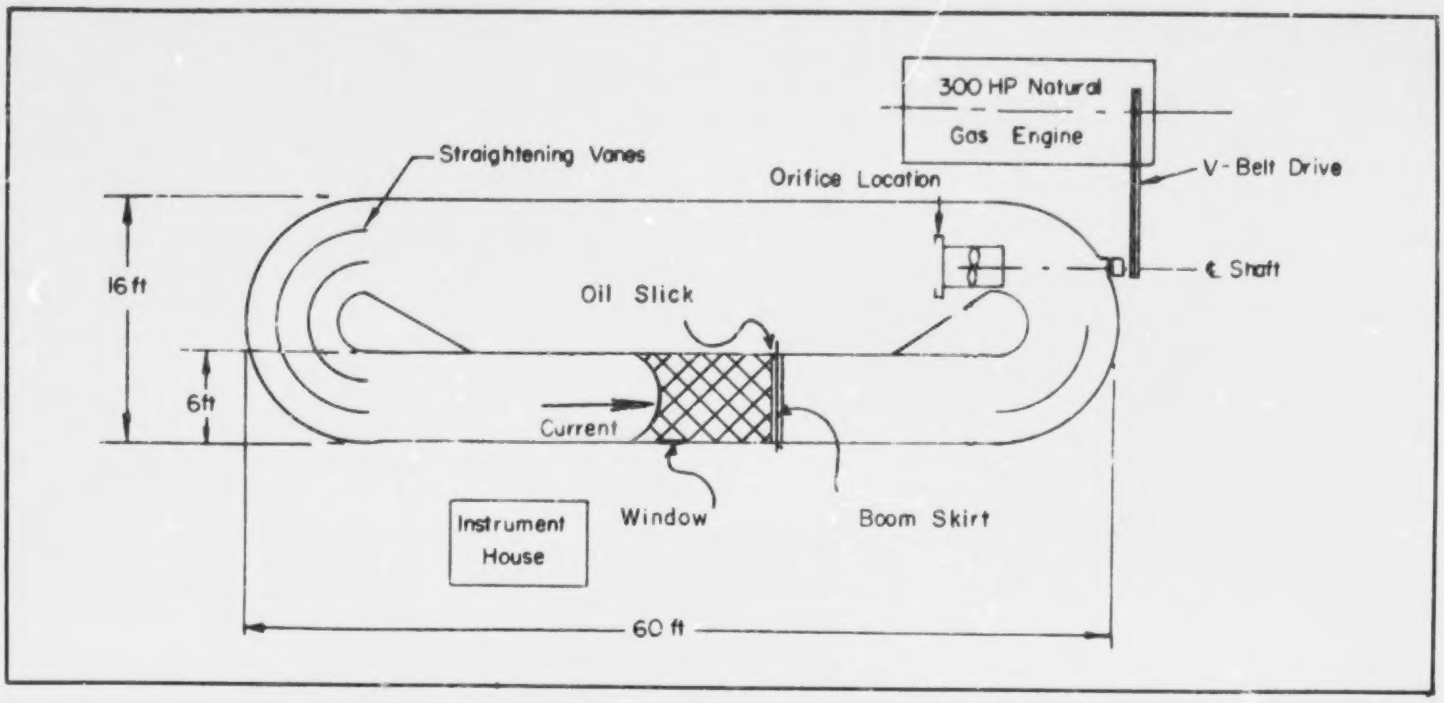


Figure 1. Plan view of experimental test tank.

the maximum drop size is related to the water flow velocity by equation (3).

Droplet motion in the flowing water phase will be discussed below (see page 58).

Region II

It is well known[12,13] that the streamlines in a flow field over an abrupt surface discontinuity separate from the surface just downstream of the discontinuity. If the bounding surface is relatively smooth and extends far enough downstream, the streamlines re-attach themselves to the surface. This phenomenon is called boundary layer separation and re-attachment.

In the present case the surface discontinuity is the head wave discussed above. The distance downstream at which re-attachment occurs can be estimated from Plate's work[14] with abrupt surface roughnesses in a turbulent boundary layer. Plate found that re-attachment occurred about 50 disturbance heights downstream. In the present case, the point of re-attachment will be chosen as 50 times the difference of the head wave amplitude and the film thickness m_I, or 50 times m_I given by equation (1). After re-attachment of the boundary layer has occurred, the flowing water causes a drag on the oil and sets up a circulation within the oil layer. A progressive thickening of the oil layer results. It is important to analyze the oil thickness in order to arrive at the length of the oil slick.

The approach taken to this aspect of the problem, presented in fuller detail in Appendix 1, can be summarized as follows:

1. Relate the circulation in the oil phase to the drag caused by the water flow by applying the Navier-Stokes equations.
2. Relate the drag on the oil to the water flow speed by employing the results of boundary layer analysis.
3. Relate the slope of the oil interface to the drag by using a force balance.

The mathematical results obtained using this approach are summarized below:

Oil circulation

For flow conditions where the following inequality is satisfied:

$$\left(\frac{\overline{m}_{II}}{x_{II} - x_{I}}\right) \left(\frac{\overline{m}_{II}\overline{u}_{iII}\,\rho_o}{\mu_o}\right) < 1 \qquad (4)$$

The Navier-Stokes equation can be simplified to give the relationship between the interfacial velocity and the interfacial shear stress:

$$u_i = \frac{\tau_i\, g_c}{\mu_o} \quad \frac{m}{2} \qquad (5)$$

Drag on the Oil

Boundary layer theory can be used to get the local shear stress caused by the water flow:

$$\tau_i = \frac{\rho_w\,(U_\infty - u_i)^2}{2g_c} \; C_F' \qquad (6)$$

where C_F depends on the flow conditions, as discussed in Appendix 1.

Interfacial slope

A force balance in the horizontal direction shows that the slope of the interface must just balance the interfacial shear stress:

$$\tau_i = \rho_o \frac{g_L}{g_c} \; m \frac{\Delta m}{\Delta x} \qquad (7)$$

The relations above provide a set of three simultaneous, independent, non-linear, ordinary differential equations for the three dependent variables m, μ_i, and τ_i. They may be solved using the numerical technique described in Appendix 1. The starting value of x is the point of boundary layer re-attachment, $50m_I$ down stream of the head wave. The starting value of m is m_I.

Using the program listed in Appendix 1, calculations were made for oil film thickness and cumulative oil slick volume as a function of distance from the start of the slick for a variety of water current speeds and oil properties. The results of these calculations are presented in Figures 5 to 18.

The formation of waves at the oil-water interface in Region II was observed to correspond fairly well with the predictions of Kelvin-Helmholtz instability,[15,16] which predicts a critical velocity U_c for wave formation as follows.

$$U_c = \frac{1 + \rho_o/\rho_w}{\sqrt{\rho_o/\rho_w}} \sqrt{\frac{1 - \rho_o/\rho_w}{1 + \rho_o/\rho_w} \; 2\sqrt{\frac{g_L \, \sigma \, g_c}{\rho_w - \rho_o}}} \tag{8}$$

where σ is the oil-water interfacial tension.

Region III

In the immediate region of the boom, say nearer than about five times the skirt immersion under the oil, the flow in both phases is different from the predictions of the simplified model developed for Region II.

Flow in the oil phase is not as readily calculable because the assumptions made in arriving at the Region II equations are no longer valid. The length of this region will be assumed, as stated above, as

$$x_{III} - x_{II} = 5\,(S - m\,(x_{II})) \tag{9}$$

and the film thickness will be assumed constant

$$m\,(x) = m\,(x_{II}) = const \tag{10}$$

in Region III, with negligible effect on the accuracy of the slick length calculation.

Flow in the water phase very likely follows the predictions of the potential flow model as described, for example, in References 17 and 18. The equations for the potential functions ϕ and the stream function ψ are

$$\phi^2 - \frac{U^4 x^2 y^2}{\phi^2} = U^2\,(x^2 - y^2 + \ell^2) \tag{11}$$

$$\frac{U^4 x^2 y^2}{\psi^2} - \psi^2 = U^2\,(x^2 - y^2 + \ell^2) \tag{12}$$

where $\ell = s - m_{II}$.

The velocities in the x and y directions are u and v, respectively, found by differentiation of ϕ or ψ:

$$u = \frac{\partial \psi}{\partial y} = \frac{\partial \phi}{\partial x} \tag{13}$$

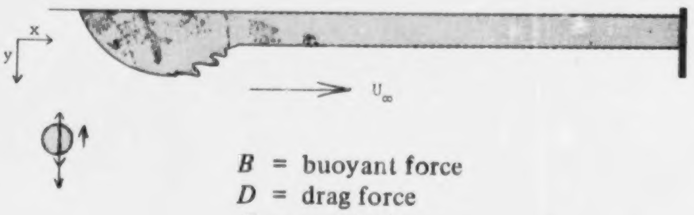
$$v = -\frac{\partial \psi}{\partial x} = \frac{\partial \phi}{\partial y} \tag{14}$$

These equations show that farther than about 5ℓ from the boom the velocity v in the water is very small. Closer than about 5ℓ to the boom; however, these equations show that any oil droplet still present in the flowing water will be swept under the boom with the water.

Droplet Motion as a Mode of Failure

Once the droplet is entrained into the water current, it experiences certain forces which dictate its subsequent motion. If these forces result in a net upward motion of the drop, it may coalesce into the oil layer at the surface. If the forces result in either a net downward motion or no net motion vertically, the droplet will be swept along with the water and flow under the boom.

The vertical forces which act on the oil drop are indicated in the sketch below:



B = buoyant force
D = drag force
G = gravity force
S = sidewise force (negative lift force)

A description of how these forces are evaluated is presented in Appendix 2. The force S is negligible under certain conditions, discussed in Appendix 2, and its absence greatly simplifies the analysis.

The sum of these forces is related to the acceleration of the droplet; substituting for the forces and simplifying yields the equation:

$$1 - \frac{\rho_w}{\rho_o} - \frac{3}{4}\frac{C_D}{g_L d}\frac{\rho_w}{\rho_o}\,(v_p - v_F)\,|(v_p - v_F)| = \frac{U_\infty}{g_L}\left(1 + \frac{\rho_w}{2\rho_o}\right)\frac{dv_p}{dx} \tag{15}$$

The term v_F is the transverse velocity downward caused by growth of the boundary layer thickness, as derived in Appendix 2. The drag coefficient C_D is obtained from the correlation of Hu and Kintner.[19]

Knowing an initial velocity and reference position, equation (15) can be solved numerically to yield the vertical particle velocity as a function of distance downstream from the point of drop formation. Integration of the velocity, in turn, yields the vertical position of the droplet as a function of distance. In Appendix 2, solutions of equation (15) are presented which show that the oil droplets reach their terminal rise velocity in water very quickly, even after being given an initial downward component of velocity when being torn off the head wave. A

TABLE 2 - Calculated Terminal Velocities

a. Interfacial Tension = 10 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity .8	.85	.9	.95	.97	.98	.99
0.0010	0.003566	0.002916	0.002195	0.001351	0.000945	0.000711	0.000438
0.0020	0.007133	0.005832	0.004391	0.002703	0.001890	0.001423	0.000876
0.0040	0.014266	0.011664	0.008782	0.005406	0.003781	0.002846	0.001752
0.0065	0.023183	0.018955	0.014271	0.008785	0.006144	0.004626	0.002847
0.0100	0.035668	0.029162	0.021956	0.013516	0.009452	0.007117	0.004381
0.0200	0.071317	0.058317	0.043911	0.027032	0.018906	0.014234	0.008762
0.0400	0.141914	0.116273	0.087688	0.054041	0.037806	0.028467	0.017525
0.0650	0.223815	0.185383	0.141099	0.087549	0.061357	0.046231	0.028473
0.1000	0.307306	0.263190	0.207284	0.132567	0.093750	0.070878	0.043759
0.2000	0.369552	0.339260	0.295863	0.221511	0.170109	0.134129	0.085882
0.4000	0.000000	0.000000	0.000000	0.252218	0.218110	0.190420	0.142903
0.6500	0.000000	0.000000	0.000000	0.000000	0.000000	0.195046	0.161475
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.159074

b. Interfacial Tension = 20 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity .8	.85	.9	.95	.97	.98	.99
0.0010	0.003327	0.002720	0.002048	0.001261	0.000882	0.000664	0.000409
0.0020	0.006655	0.005441	0.004096	0.002522	0.001764	0.001328	0.000817
0.0040	0.013310	0.010883	0.008193	0.005044	0.003527	0.002656	0.001635
0.0065	0.021630	0.017685	0.013315	0.008196	0.005732	0.004316	0.002657
0.0100	0.033278	0.027209	0.020485	0.012610	0.008819	0.006640	0.004087
0.0200	0.066551	0.054416	0.040971	0.025221	0.017639	0.013280	0.008175
0.0400	0.132791	0.108678	0.081887	0.050435	0.035277	0.026561	0.016351
0.0650	0.212642	0.174993	0.132451	0.081841	0.057293	0.043151	0.026569
0.1000	0.306552	0.257795	0.199049	0.124954	0.087860	0.066280	0.040856
0.2000	0.411404	0.371929	0.316105	0.224870	0.166831	0.128913	0.080979
0.4000	0.000000	0.000000	0.342575	0.283933	0.239408	0.203749	0.145302
0.6500	0.000000	0.000000	0.000000	0.000000	0.246480	0.221535	0.177680
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.182599

c. Interfacial Tension = 30 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity .8	.85	.9	.95	.97	.98	.99
0.0010	0.003194	0.002611	0.001966	0.001210	0.000846	0.000637	0.000392
0.0020	0.006389	0.005223	0.003933	0.002421	0.001693	0.001275	0.000785
0.0040	0.012778	0.010447	0.007866	0.004842	0.003386	0.002549	0.001569
0.0065	0.020765	0.016978	0.012782	0.007868	0.005503	0.004143	0.002550
0.0100	0.031948	0.026121	0.019666	0.012106	0.008466	0.006374	0.003924
0.0200	0.063894	0.052242	0.039334	0.024213	0.016934	0.012749	0.007848
0.0400	0.127600	0.104392	0.078636	0.048422	0.033868	0.025500	0.015697
0.0650	0.205385	0.168641	0.127405	0.078617	0.055016	0.041431	0.025508
0.1000	0.302108	0.251981	0.193011	0.120358	0.084467	0.063675	0.039231
0.2000	0.433290	0.387498	0.323712	0.223538	0.163156	0.125044	0.078010
0.4000	0.000000	0.409167	0.370111	0.301460	0.249643	0.208851	0.144561
0.6500	0.000000	0.000000	0.000000	0.301918	0.265958	0.236749	0.185595
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.233599	0.196671

d. Interfacial Tension - 40 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity .8	.85	.9	.95	.97	.98	.99
0.0010	0.003104	0.002538	0.001911	0.001176	0.000823	0.000619	0.000381
0.0020	0.006209	0.005076	0.003822	0.002353	0.001645	0.001239	0.000763
0.0040	0.012419	0.010153	0.007644	0.004706	0.003291	0.002473	0.001525
0.0065	0.020181	0.016500	0.012423	0.007647	0.005348	0.004027	0.002479
0.0100	0.031049	0.025386	0.019113	0.011765	0.008228	0.006195	0.003813
0.0200	0.062098	0.050773	0.038227	0.023532	0.016457	0.012391	0.007627
0.0400	0.124065	0.101483	0.076434	0.047062	0.032916	0.024783	0.015256
0.0650	0.200198	0.164199	0.123937	0.076427	0.053475	0.040268	0.024790
0.1000	0.297655	0.247139	0.188509	0.117160	0.082147	0.061905	0.038132
0.2000	0.446685	0.396188	0.326847	0.221364	0.160068	0.122147	0.075942
0.4000	0.463371	0.432937	0.389363	0.312749	0.255406	0.211015	0.143226
0.6500	0.000000	0.000000	0.000000	0.319628	0.279508	0.246891	0.190127
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.247583	0.206388

further simplification was found: ν_F was shown to be negligible compared to the terminal rise velocity ν_t for all but the very smallest drops; however, since they are more prevalent at higher velocities these small drops will flow under the boom anyway, as discussed below. Equation (15) can be reduced to a cubic polynomial, the real root of which is ν_t. Calculations of ν_t were made over a wide range of conditions, and the results are shown in Table 2.

The drop must rise a certain distance Δy in order to coalesce into the oil layer. Since the head wave is somewhat deeper than $2m_I$ below the surface and since the water flowing past will cause the drop to go slightly deeper than its point of generation, Δy will be given the value $2m_I$. The droplet trajectory is simply

$$x = y \frac{U_\infty}{\nu_t} \tag{16}$$

If the length of the slick in regions I and II is longer than

$$2\, m_I \frac{U_\infty}{\nu_t}$$

the droplet has enough time to rise and coalesce into the oil layer; if the slick is shorter than this value, the droplet will be swept under the barrier.

Calculations of the conditions under which droplet failure will occur have been made using the models presented here, and the results are summarized graphically in Figures 19 to 28. The region below the horizontal solid line is completely safe from the standpoint of droplet failure because this line is the velocity below which no droplets form; it was obtained from equations (2) and (3). The region above the sloping lines is the zone where failure by droplet entrainment is certain, since in this zone even the maximum size oil droplets (having the largest rise velocity) will escape under the barrier. (Note that the rate at which failure will occur in this region cannot be determined since the rate of droplet generation is unknown). The region between the sloping lines and the horizontal line is not as exactly defined because the size distribution of the oil droplets formed at the head wave is unknown; the smaller droplets would tend to escape, while those closer to the maximum size would coalesce into the slick, especially for the small velocity sub-regions. The dashed lines on these graphs will be discussed in the next section.

Draining as a Mode of Failure

When two immiscible liquids are placed in a tank and a drain opened at the bottom of the tank, the lower fluid will begin to flow out; at a certain height above the drain hole, the upper fluid will plunge through the lower fluid and enter the drain. A recent analysis[20] of this problem has been published. The relevance of this phenomenon to oil spill containment is clear: flow conditions could exist where oil could plunge under or drain past the boom and escape with the water.

A simple extension of the work done in Reference 20 is presented in Appendix 3. The result of the analysis is the following expression for critical skirt depth to prevent failure by this mode:

$$S_{MIN} = m_{III} + \frac{(U_\infty - u_{iIII})^2}{g_L \left(1 - \frac{\rho_{OIL}}{\rho_W}\right)} \tag{17}$$

Values of the parameters m_{III} and u_i were obtained from the analysis discussed in an earlier section of this paper.

Calculations of S_{MIN} were made for a range of conditions, and the results are presented in Figure 29. The velocities at which failure occurs for 6-inch, 12-inch, and 24-inch skirt depths are substantially independent of the amount of oil spilled. These values are indicated on Figures 19 to 28 by dashed lines.

Application to a Draped Boom in a Current

The calculations presented in this paper are based on a two-dimensional flow model of a barrier perpendicular to a current. In some cases, however, such as a large spill on the ocean, the barrier would be used in a draped configuration, shown in plan view at right.

If the boom shape resulting from the current is known or can be estimated, the two-dimensional model can be used to estimate the length, thickness, and failure characteristics of the oil slick.

Referring to the sketch (right), if the shape of the boom is given by the function $B(z)$, the problem of finding the x_o and hence z_o resulting from given conditions can be formulated as follows:

$$Q_{OIL} = 2 \int_0^{z_o} \int_{x_o}^{B(z)} m(x)\, dx\, dz \tag{18}$$

Knowing $B(z)$, x_o is assumed, and $m(x)$ found from the program and results presented earlier. Then $m(x)$ is integrated as indicated above, and Q_{OIL} is calculated. If Q_{OIL} is not equal to the known volume of spill, x_o is re-assumed and the calculation repeated. Note that if z_o exceeds $L/2$, the boom would allow oil to spill over the ends.

The boom configuration would take the shape of a catenary if the drag along the boom length were uniform; since the drag will be slightly higher in the center portions of the boom fronting directly into the current, the boom will be somewhat more peaked than the catenary. If the included angle ϕ is not too small, however, the catenary shape should be a good approximation; it will be used in the example discussed below.

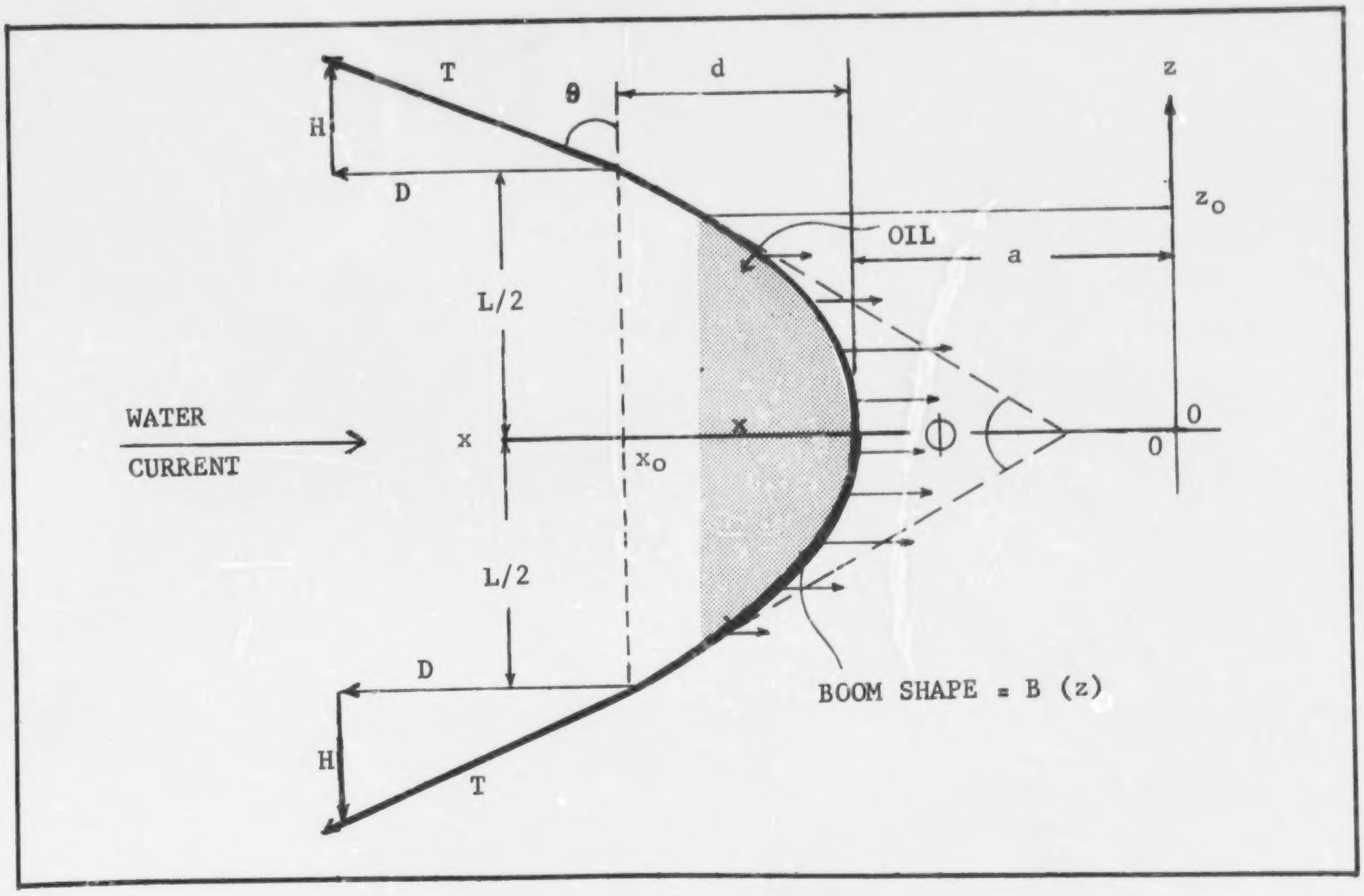
Certain properties of the catenary[21] are useful in the example calculations. These include:

boom shape

$$B(z) = a \cosh \frac{z}{a} \tag{19}$$

the sag d

$$d = a \left(\cosh \frac{L}{2a} - 1\right) \tag{20}$$



a relation between a, the span L, and boom length A

$$A = 2a \sin h \frac{L}{2a} \tag{21}$$

a relation between a, A, and d

$$a = \frac{A^2}{8d} - \frac{d}{2} \tag{22}$$

the side pull H

$$H = T \cos \theta \tag{23}$$

the drag D

$$D = T \sin \theta \tag{24}$$

where

$$a = H/w \tag{25}$$

w = drag force per unit boom length, LB_F/Ft

T = tension in the restraining cable, LB_F

$$\phi = 2\,(90^\circ - \theta) \tag{26}$$

The geometrical significance of the various terms is shown on the sketch above. The maximum area within the boom arc available for containing oil is

$$(Area)_{MAX} = L\,(a + d) - aA \tag{27}$$

The area occupied by the oil, referring to the sketch above, is

$$(Area)_{OIL} = 2\left[z_o\, B(z_o) - \int_o^{z_o} a \cos h \frac{z}{a}\, dz\right]$$

$$= 2\left[z_o\, B(z_o) - a^2 \sin h \frac{z_o}{a}\right] \tag{28}$$

The drag force w per unit length, assumed constant over the entire boom, is evaluated from

$$w = C_D S \frac{\rho_W U_\infty^2}{2g_c} \tag{29}$$

with C_D = 1.98 according to Reference 22; S in this formula is the skirt depth.

Use of these formulas is best illustrated by means of an example: 1000 barrels of 0.9 specific gravity oil with a viscosity of 81 centipoise and interfacial tension of 30 dynes per centimeter is spilled in a one knot current. A 1000 foot long boom with a 9-inch skirt is to be deployed with two boats, each capable of pulling up to 4000 LB tension. Find the length of the slick and the possible failure conditions, and consider possible better methods of operation.

1. Determine the drag per unit length w.
   From (29),

$$w = 1.98 \times \frac{9}{12} \times \frac{62.4 \times (1.69)^2}{64.4}$$

$$= 4.11 \text{ LB/FT}$$

2. Calculate the total drag on each half of the boom D.

$$D = w\frac{A}{2}$$

$$= 4.11 \times \frac{1000}{2}$$

$$= 2050 \text{ LB}$$

3. Calculate the angle θ
From (24),

$$\theta = \sin^{-1}\frac{D}{T} = \sin^{-1}\frac{2050}{4000}$$

$$= 30.87°$$

4. Calculate the side pull H.
From (23),

$$H = 4000 \times 0.858$$

$$= 3430 \text{ LB}$$

5. Determine the constant a
From (25),

$$a = \frac{3430}{4.11}$$

$$= 835 \text{ ft}$$

6. Obtain the span L
From (21),

$$1000 = 2 \times 835 \; \sin h \; \frac{L}{2 \times 835}$$

$$L = 950 \text{ ft}$$

7. Calculate the sag d
From (20),

$$d = 835 \left(\cos h \; \frac{950}{2 \times 835} - 1 \right)$$

$$= 139 \text{ ft}$$

8. Determine the maximum area for oil containment.
From (27),

$$(Area)_{\text{MAX}} = 950\,(835 + 139) - 835 \times 1000$$

$$= 90{,}000 \text{ ft}^2$$

9. Calculate the film thickness in Region I
From (1) or Figure 2,

$$m_I = \frac{(1.69)^2}{64.4\left(\frac{1}{0.9} - 1\right)}$$

$$= 0.399 \text{ ft}$$

10. Calculate the maximum amount of oil the boom could contain if m were constant:

$$Q_{\text{MAX}} = (Area)_{\text{MAX}} \times m_I$$

$$= \frac{90{,}000 \times 0.399}{5.61}$$

$$= 6{,}400 \text{ bbl } Q_{\text{OIL}}$$

11. Obtain z_o and x_o

a. Assume $z_o = 300$ ft

$$B(z_o) = 835 \times \cos h \; \frac{300}{835}$$

$$= 889 \text{ ft}$$

Maximum slick length = 889 - 835

= 54 ft

Figure 9 shows that m is substantially constant at m_I in the range 0 - 54 ft
From (28)

$$Q_{\text{CAL}} = (Area)_{\text{OIL}} \; m_I$$

$$= 2\left[\,300 \times 889 - (835)^2 \; \sin h \; \frac{300}{835}\,\right] 0.399$$

$$= 8770 \text{ ft}^3$$

$$= 1560 \text{ BBL}$$

b. Assume $z_o = 240$ ft

$$B(z_o) = 835 \; \cos h \; \frac{240}{835}$$

$$= 870 \text{ ft}$$

$$Q_{\text{CAL}} = 2\left[\,240 \times 870 - 835^2 \; \sin h \; \frac{240}{835}\,\right] 0.399$$

$$= 3990 \text{ ft}^3$$

$$= 711 \text{ BBL}$$

c. Assume $z_o = 255$ ft

$$B(z_o) = 835 \; \cos h \; \frac{255}{835}$$

$$= 874$$

$$Q_{\text{CAL}} = 2\left[\,255 \times 874 - 835^2 \; \sin h \; \frac{255}{835}\,\right] 0.399$$

$$= 5590 \text{ ft}^3$$

$$= 995 \text{ BBL}$$

Interpolating, $z_o = 256$ ft

$$x_o = B(z_o) = 874 \text{ ft}$$

12. Determine the failure mechanism, if any.

a. From Figure 4

$$d_{MAX} = 0.10\text{-inch}$$

b. From Table 2,

$$v_t = 0.193 \text{ ft/sec}$$

c. From (16),

$$\Delta x = 2m_l \times \frac{U_\infty}{v_t}$$

$$= 2 \times 0.399 \times \frac{1.69}{0.193}$$

$$= 7.05 \text{ ft}$$

d. At the ends where the slick is

$$7.05 + \frac{1}{12}(9 - 4.79) \times 5 = 8.8 \text{ ft}$$

in length (including Region III), or less, failure occurs by the droplet entrainment mechanism. The Δz corresponding to 8.8 ft is:

$$876 - 8.8 = 835 \cosh \frac{z}{835}$$

$$z = 234 \text{ ft}$$

$$\Delta z = 256 - 234$$

$$= 22 \text{ ft},$$

i.e., over 22 ft on each end of the boom the droplets escape.

13. The loss rate could be reduced by lowering the tension and increasing the sag. Note that a limit is eventually reached, however, where either draining failure would occur or the oil area would exceed that available, as given by (27). Another alternative is to let the boom drift down-current in order to minimize oil losses during skimming. For this to be effective, however, the increased oil area at the lower relative velocity must not exceed the available maximum, given by (27).

(Note that the maximum possible area can be determined by differentiating (27) with respect to a, using (20) and (21), and solving the resulting equation set equal to zero for A/a.)

LIST OF SYMBOLS

A = total length of the boom, ft
a = catenary scale factor defined by equation (25), ft
B = buoyant force, LB_F
$B(z)$ = boom shape, a function of z
C_D = drag coefficient dimensionless
C'_F = coefficient of local boundary layer friction, dimensionless
D = drag force, LB_F
d = drop size, ft
sag of a catenary, ft
G = gravity force, LB_F
g_c = constant = 32.174 $LB_M FT/LB_F SEC^2$
g_L = local gravitational acceleration, FT/SEC^2
H = side pull in the boom tension, LB_F
L = span of the catenary, FT
ℓ = difference in skirt depth and oil film thickness at the boom, FT
m = oil film thickness, FT
$\bar{m}$ = average value of m, FT
P = property grouping defined by equation (48), dimensionless
Q_{OIL} = volume of oil spilled, FT^3
R = boundary layer Reynolds number, dimensionless
Re = droplet Reynolds number, dimensionless
S = skirt depth, FT
sidewise force on oil droplet, LB_F
T = tension in boom, LB_F
u = velocity in the x-direction, FT/SEC
u_i = interfacial velocity, FT/SEC
U_c = water velocity FT/SEC, above which no drops exist with diameter d or larger, as given by equation (3)
U_∞ = water current speed far from the oil layer, FT/SEC
v = velocity in the y-direction, FT/SEC
v_P = oil droplet velocity downward, FT/SEC
v_F = water velocity downward, FT/SEC
w = drag force per unit length of boom, LB_F/FT
We = Weber number, the ratio of intertial to surface tension forces, dimensionless
x = horizontal distance, FT, in the direction of the current
x_o = distance of the edge of the oil slick from the origin of the coordinate system (see the catenary shaped boom sketch), FT
y = distance downward, FT
z = distance perpendicular to y and x
z_o = 1/2 of the span of the oil slick, FT

GREEK SYMBOLS

δ = boundary layer thickness, FT
θ = tension angle at the end of the boom (see the catenary shaped boom sketch), degrees
μ = liquid viscosity, $LB_M/FT/SEC$
π = 3.14159
ρ = liquid density, LB_M/FT^3
$\Delta\rho$ = water density minus oil density, LB_M/FT^3
σ = oil-water interfacial tension, LB_F/FT
τ = shear stress, LB_F/FT^2
ϕ = drape angle = $2(90 - \theta)$, degrees
also velocity potential, FT^2/SEC
ψ = stream function, FT^2/SEC

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APPENDIX 1 - REGION II ANALYSIS

An analysis has been made to permit calculation of oil spill thickness distribution and length for given values of oil volume per foot of barrier length, oil viscosity and density, and water velocity.

Approach

The approach taken to this analysis can be summarized as follows:•

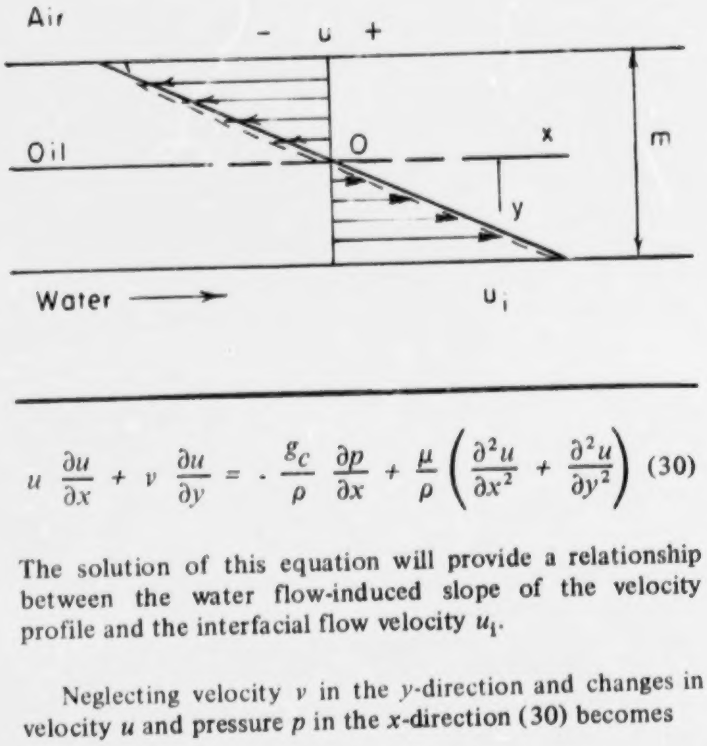
1. Relate the circulation in the oil phase to the drag caused by the water flow by applying the Navier Stokes equations.
2. Relate the drag on the oil to the water flow speed by employing the results of boundary layer analysis.
3. Relate the slope of the oil interface to the drag by using a force balance.

Navier-Stokes Equation

For an oil spill whose thickness m does not change rapidly with horizontal distance x the dashed line in the sketch (right) depicts how the velocity u is expected to vary with vertical position y.

Note that there must be a reverse flow in the upper region of the oil to balance out the flow caused by water drag.

The Navier-Stokes equation for steady flow in the x-direction is:



$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = - \frac{g_c}{\rho} \frac{\partial p}{\partial x} + \frac{\mu}{\rho} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \quad (30)$$

The solution of this equation will provide a relationship between the water flow-induced slope of the velocity profile and the interfacial flow velocity u_1.

Neglecting velocity v in the y-direction and changes in velocity u and pressure p in the x-direction (30) becomes

$$0 = \frac{\mu}{\rho} \frac{\partial^2 u}{\partial y^2} \quad (31)$$

(text continued on page 96)

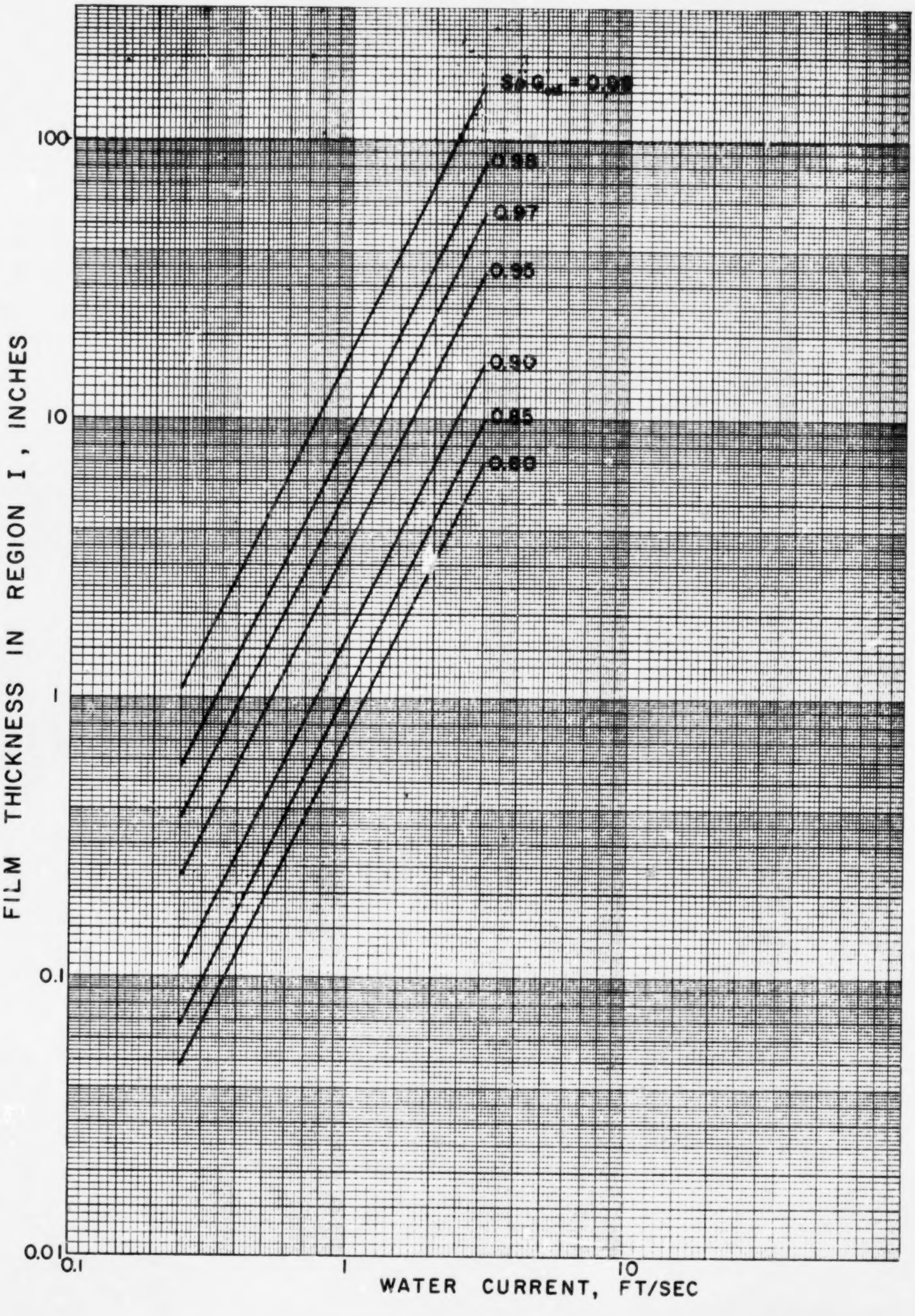


Figure 2. Oil film Thickness in Region 1.

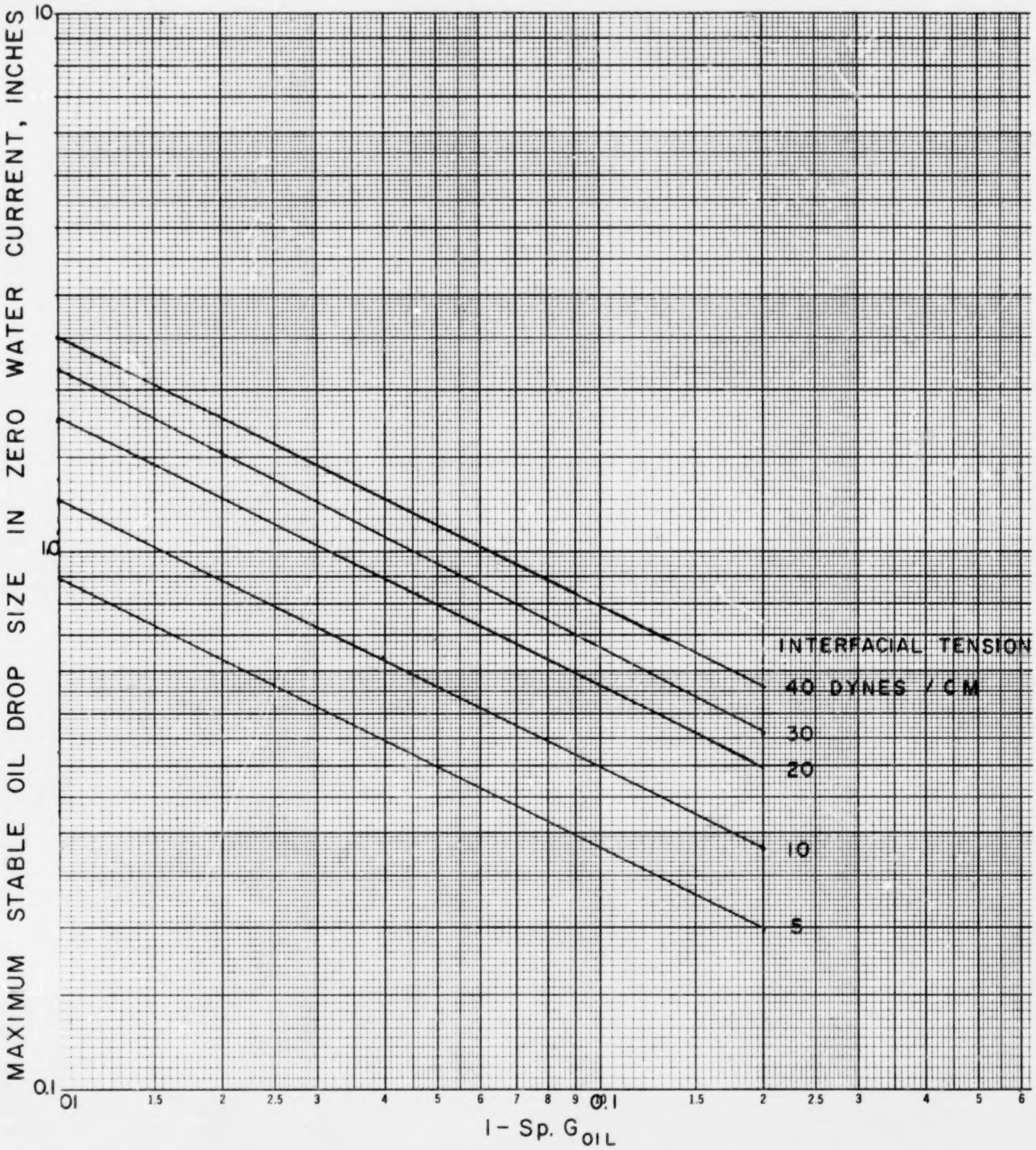


Figure 3. Predictions of maximum stable drop size according to equation 2.

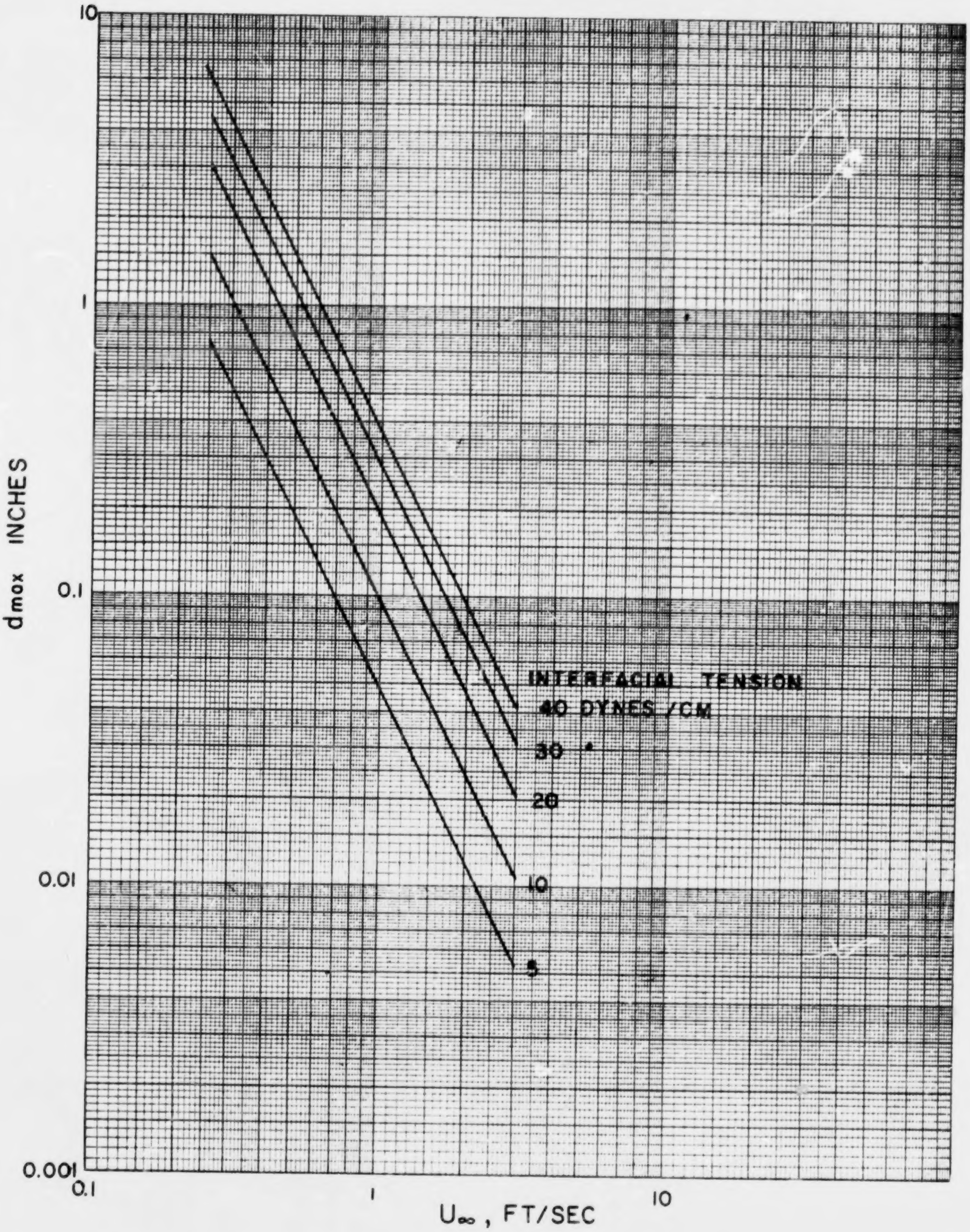


Figure 4. Effects of water current and interfacial tension on maximum oil drop size.

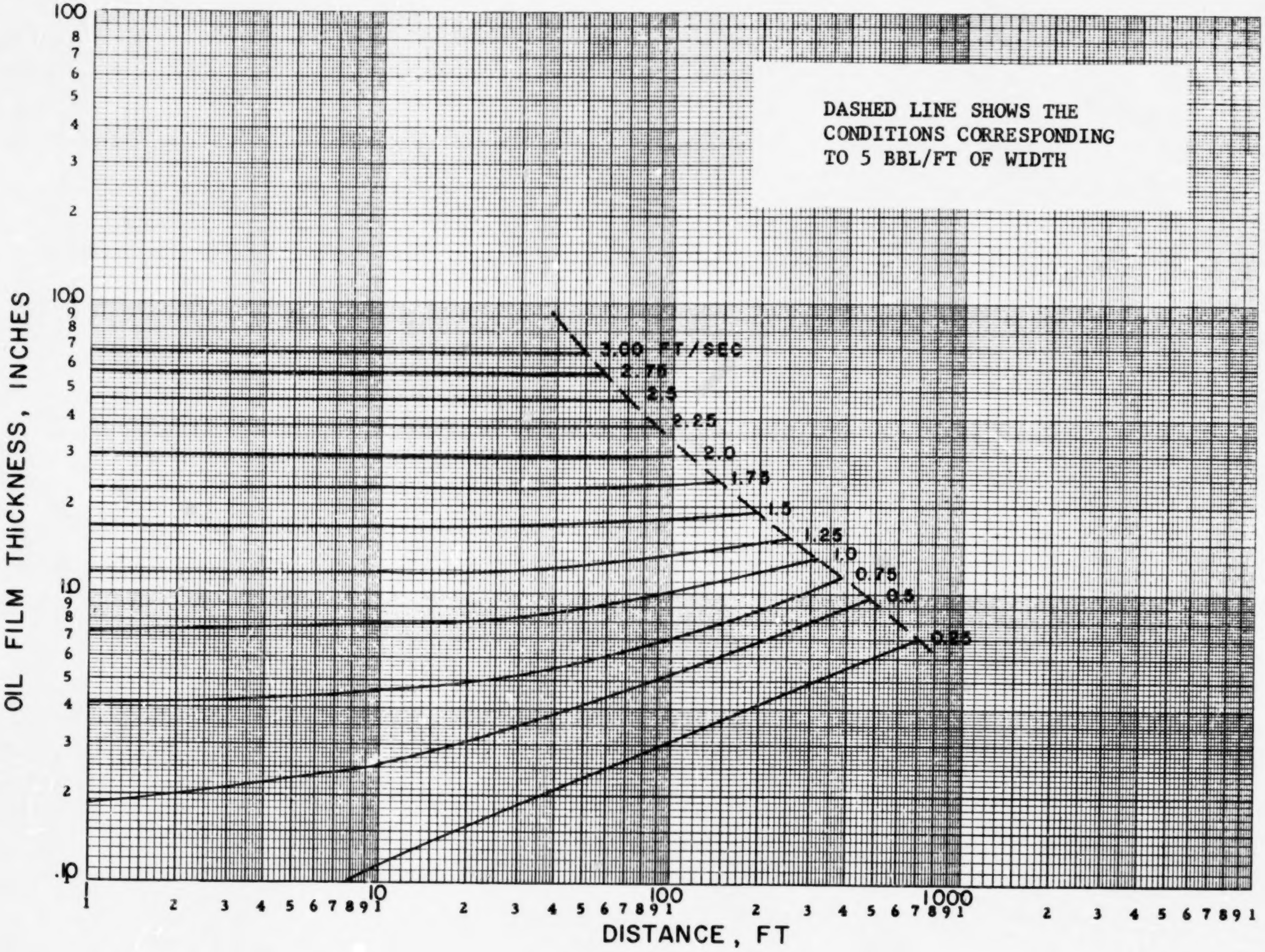


Figure 5. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.80, μ = 2.56 cp.

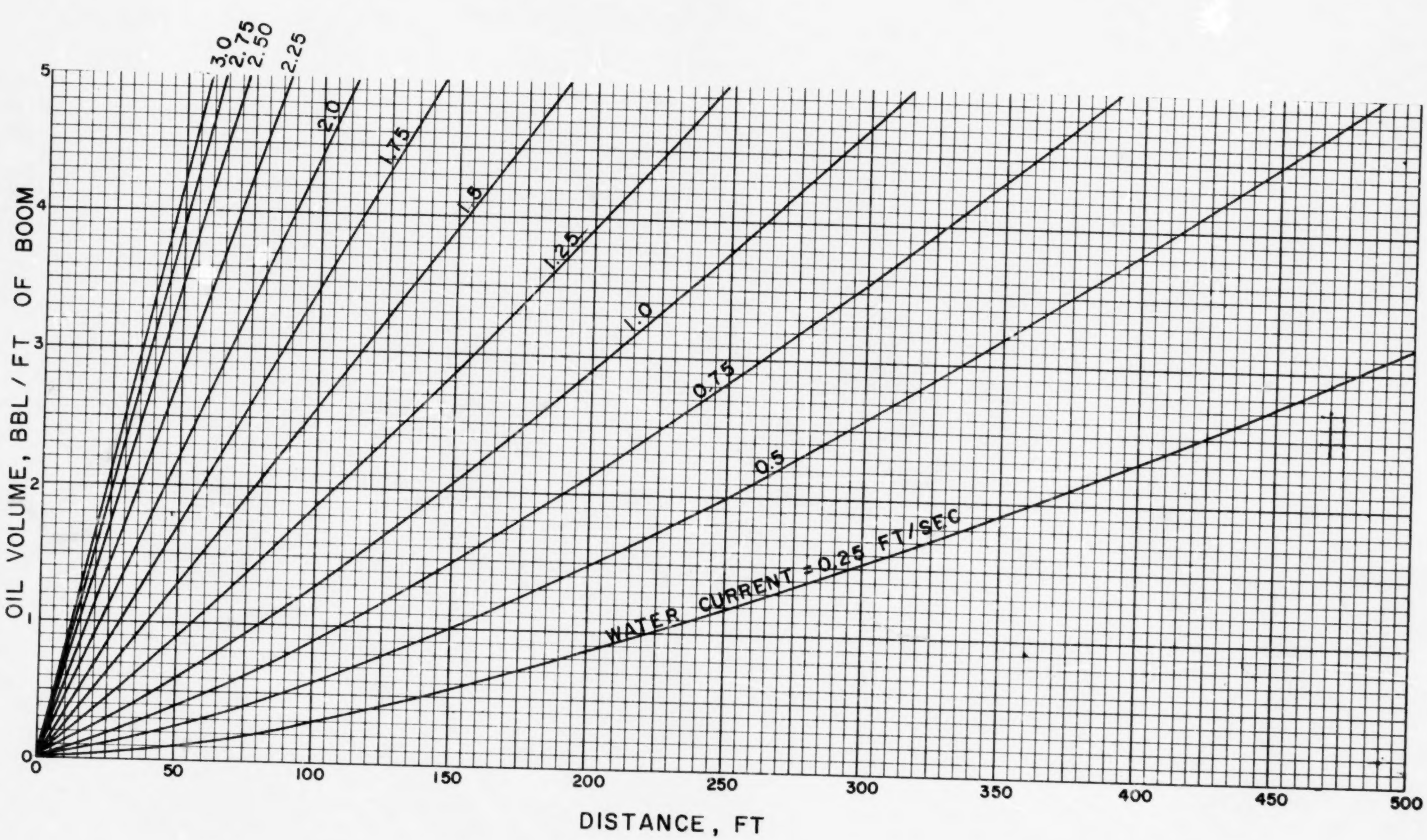


Figure 6. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.80, μ = 2.56 cp.

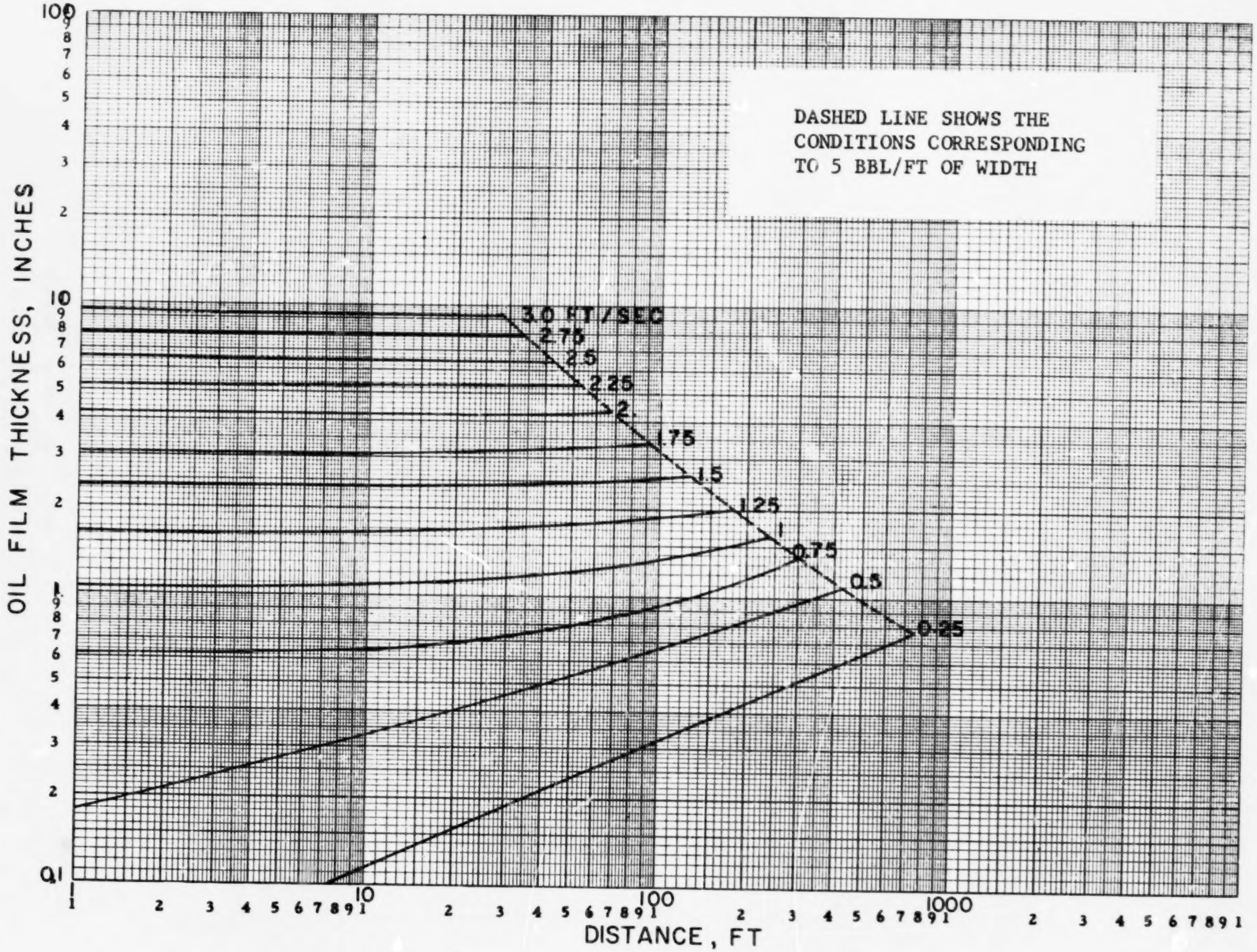


Figure 7. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.85, $\mu = 10.37$ cp.

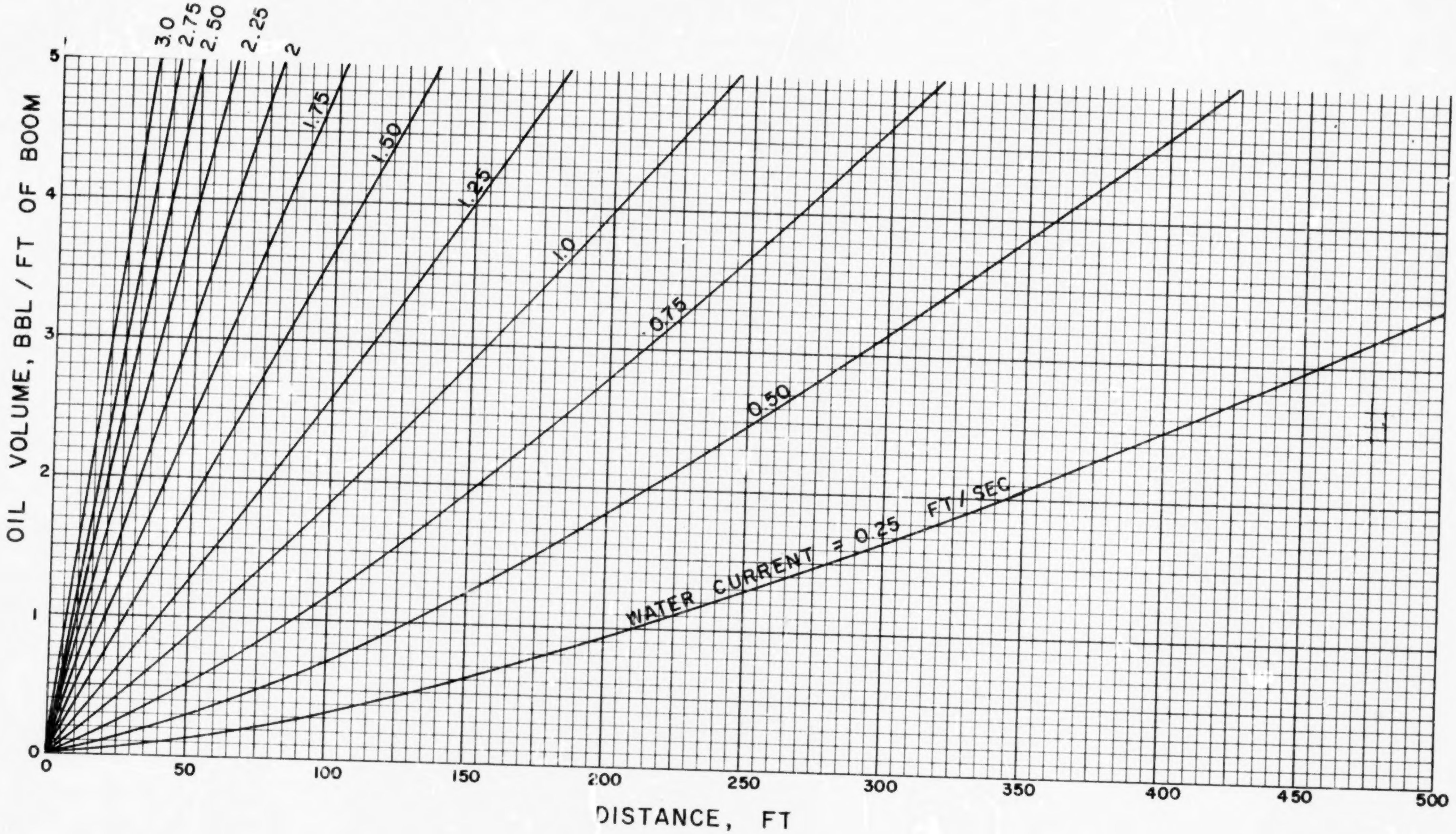


Figure 8. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.85, μ = 10.37 cp.

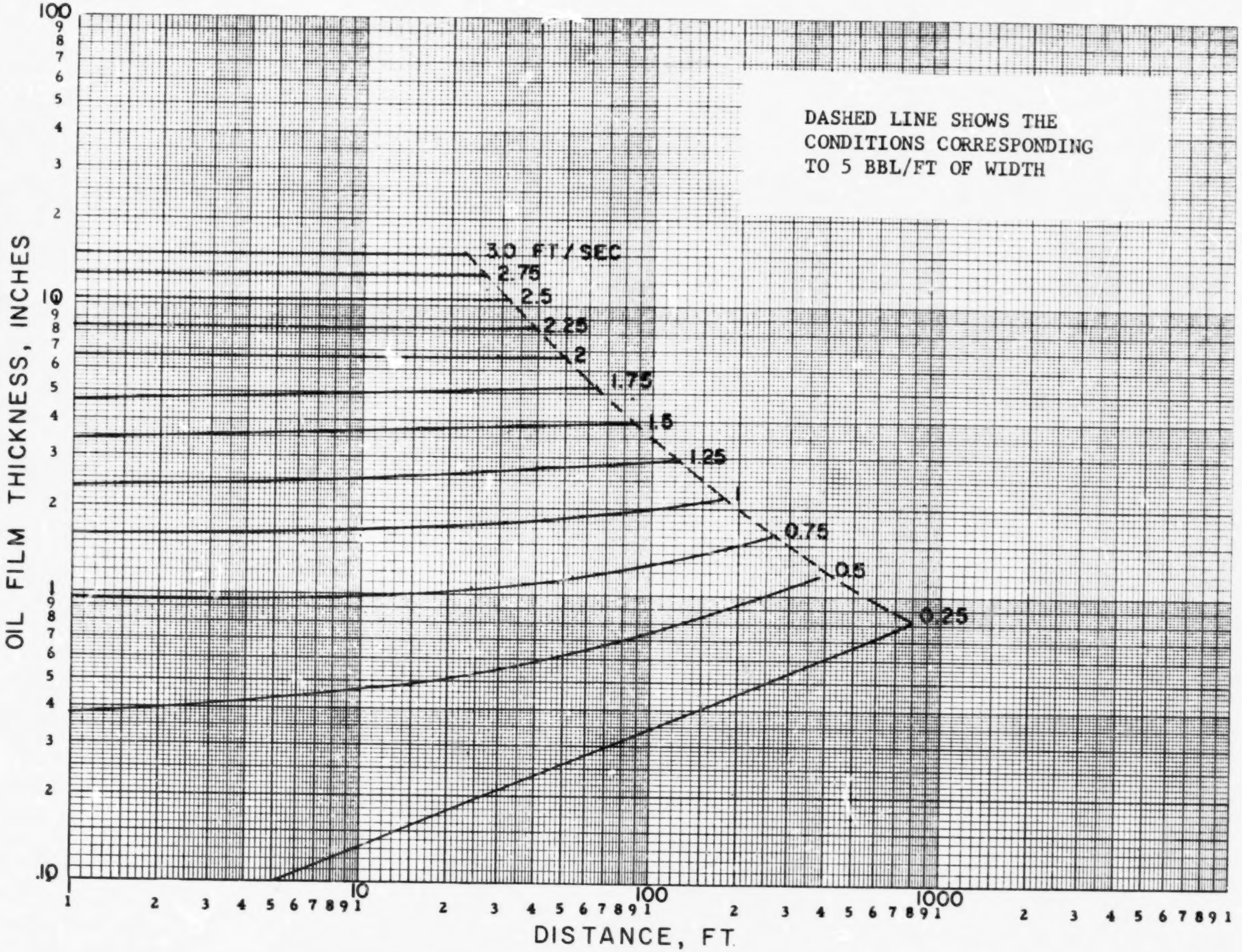


Figure 9. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.90, μ = 81 cp.

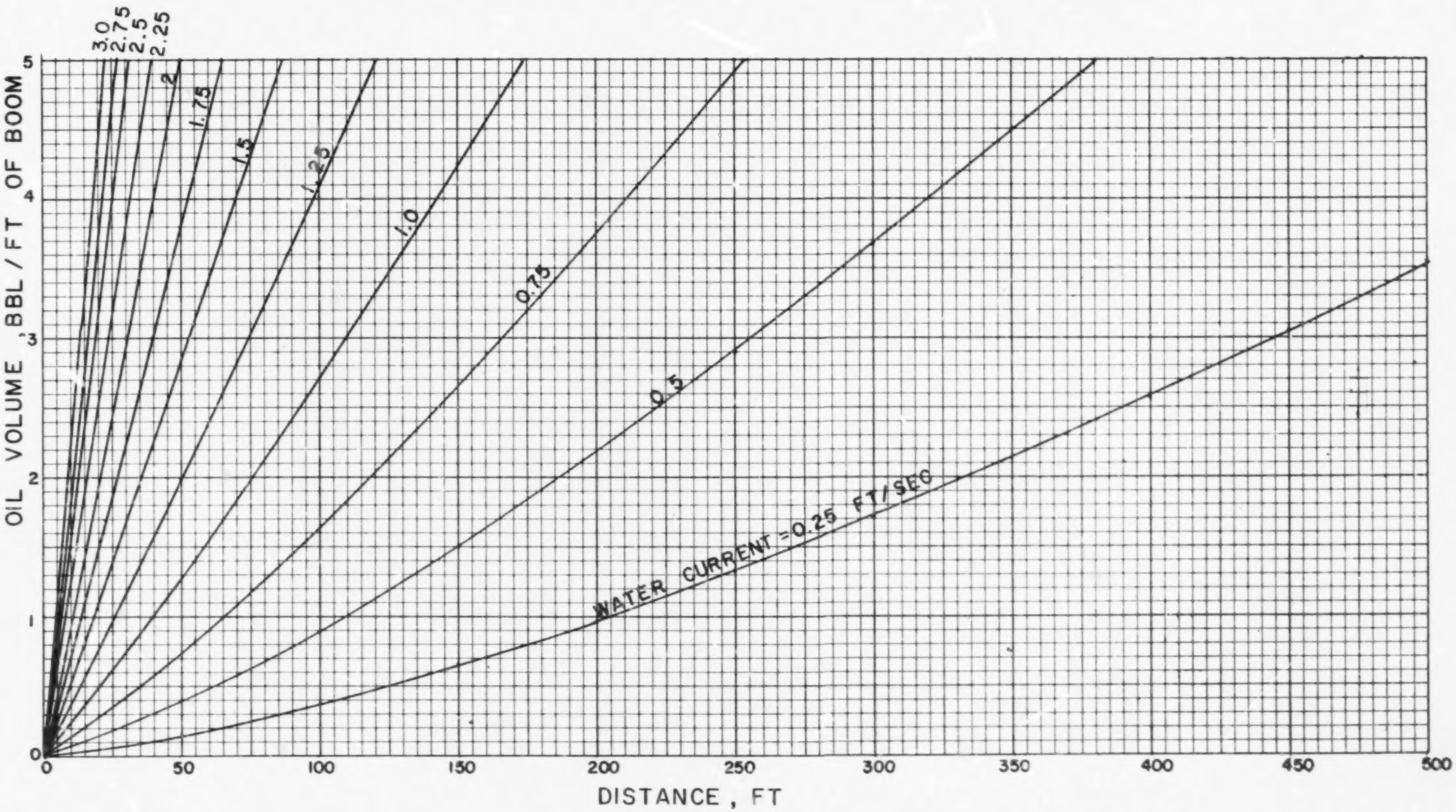


Figure 10. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.90, $\mu = 81$ cp.

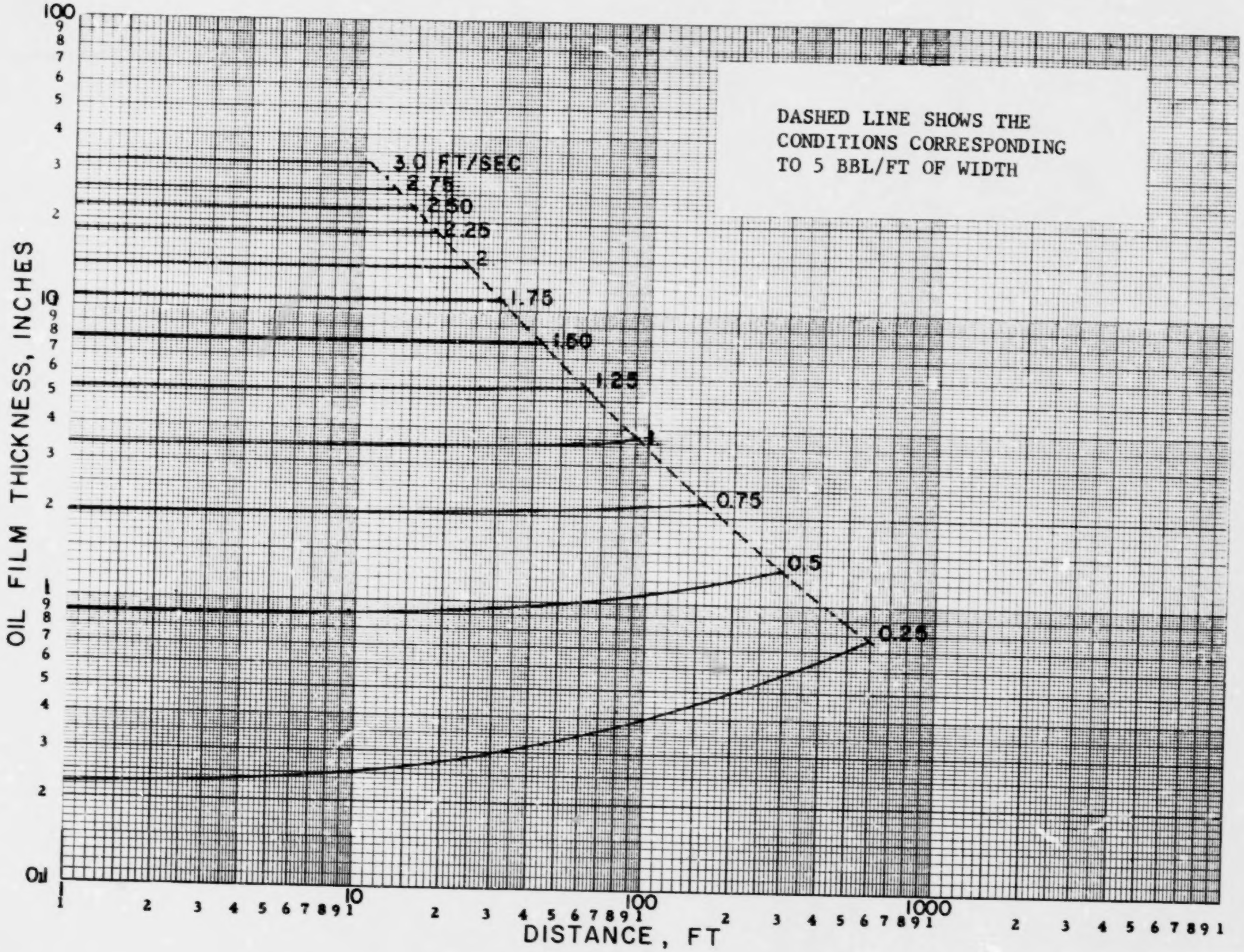


Figure 11. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.95, μ = 1,805 cp.

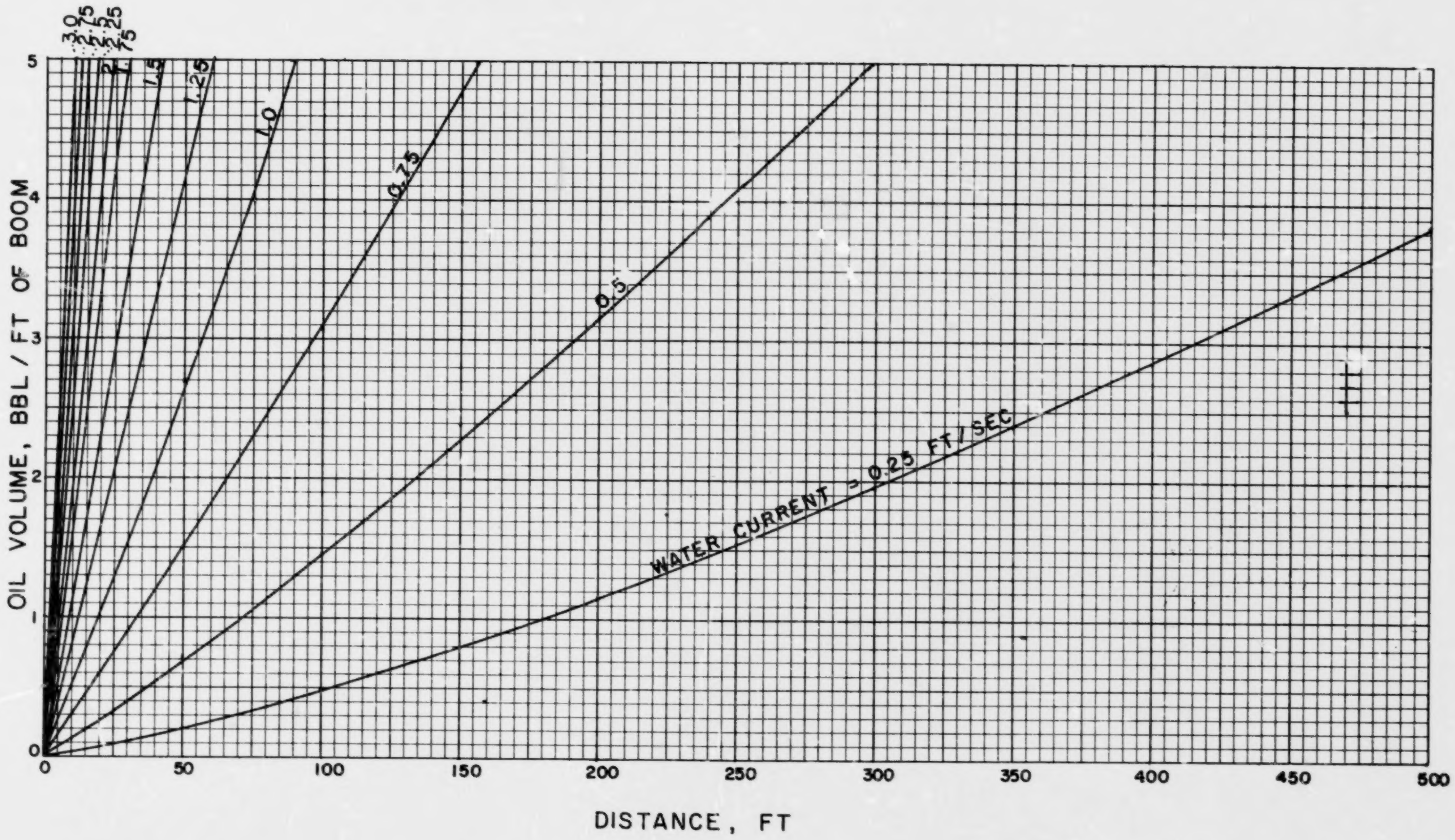


Figure 12. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.95, μ = 1,805 cp.

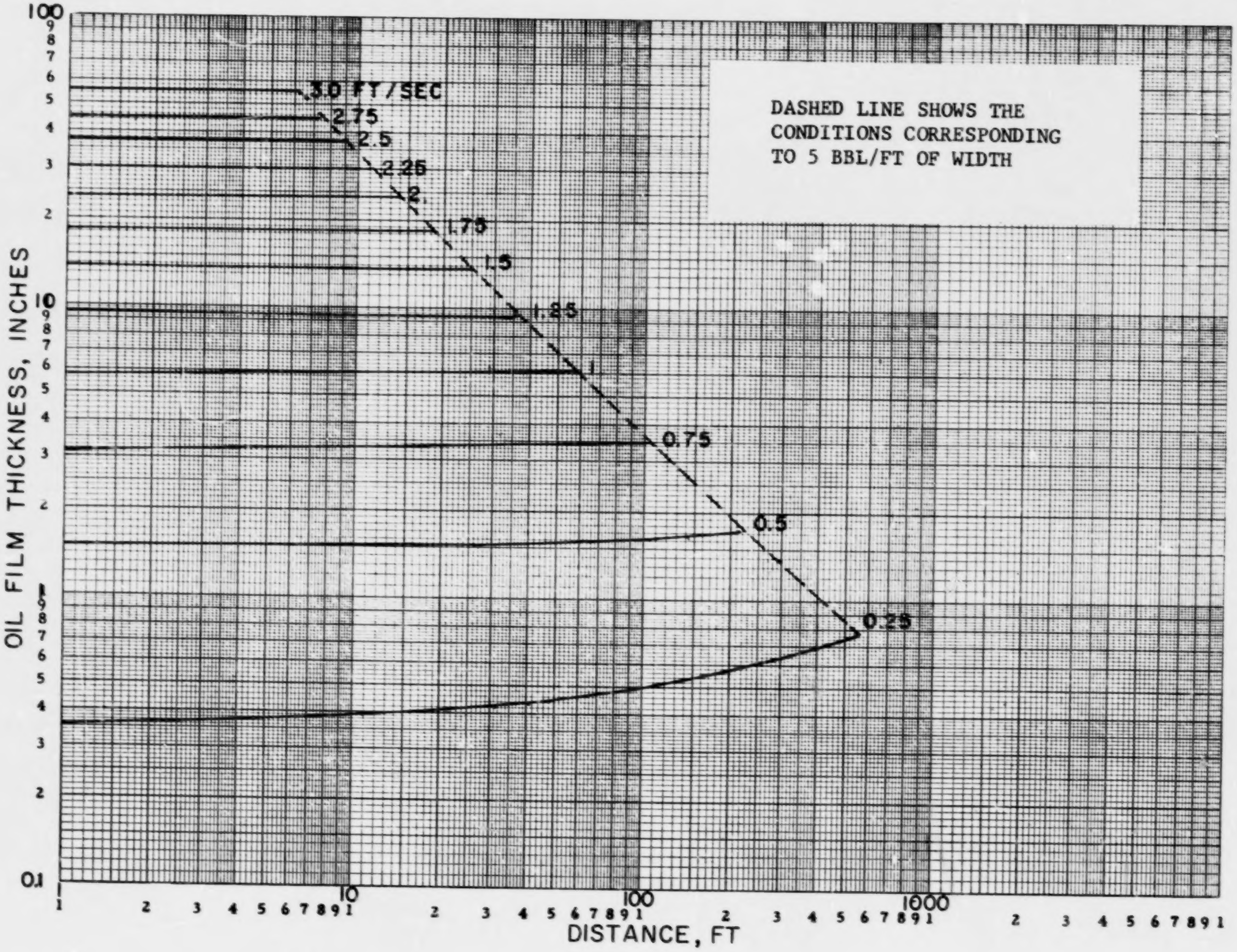


Figure 13. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.97, μ = 9.215 cp.

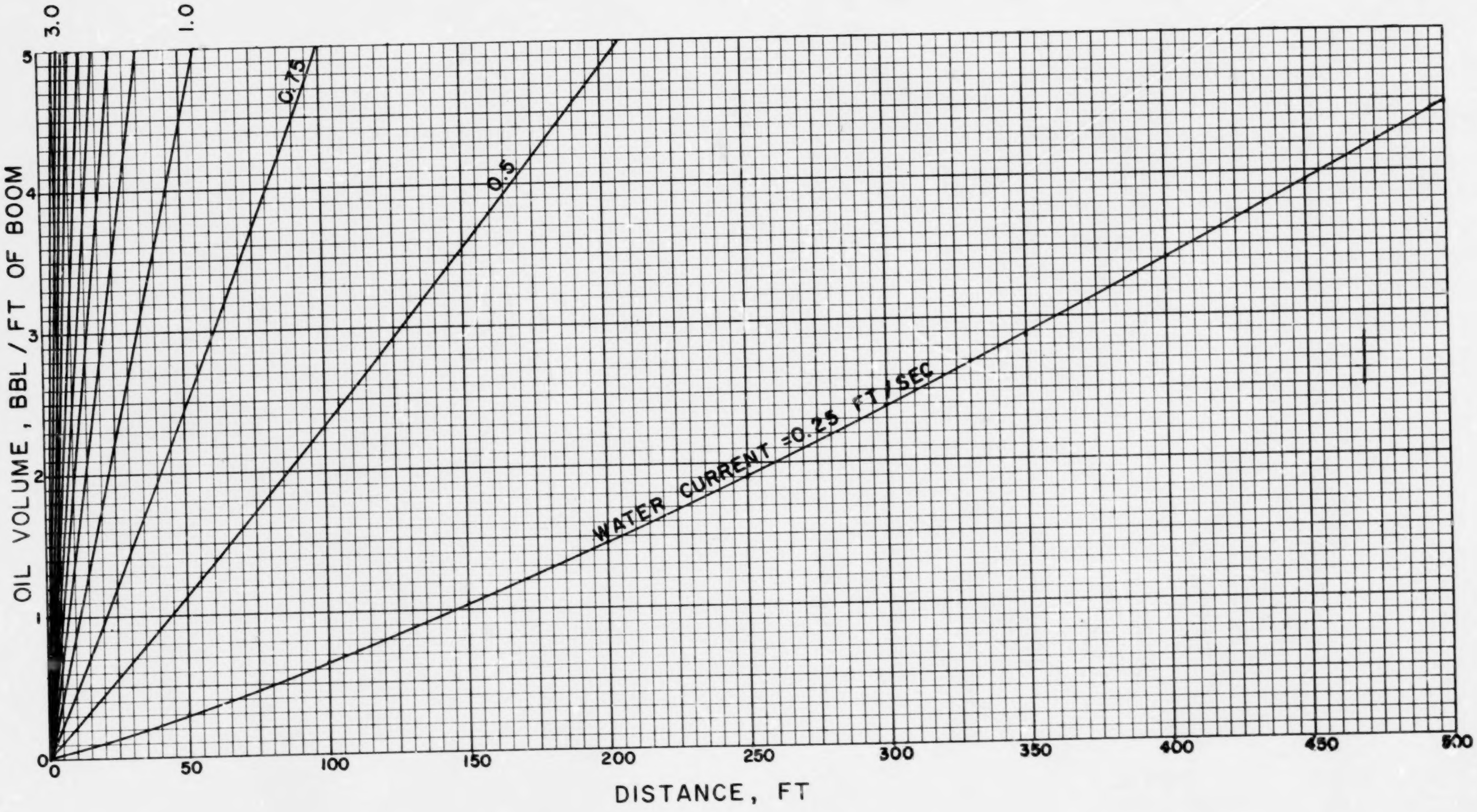


Figure 14. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.97, μ = 9,215 cp.

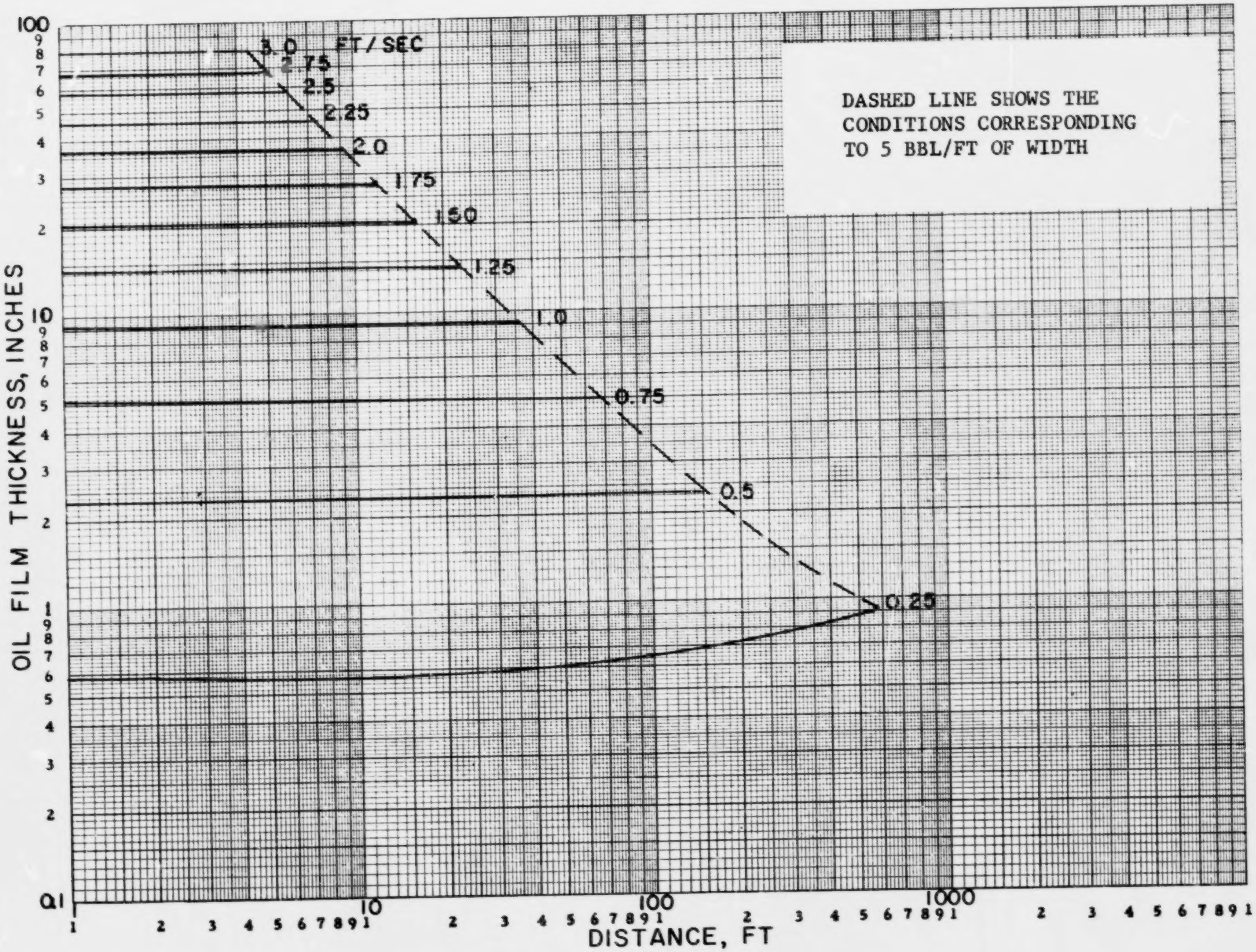


Figure 15. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.98, μ = 23,520 cp.

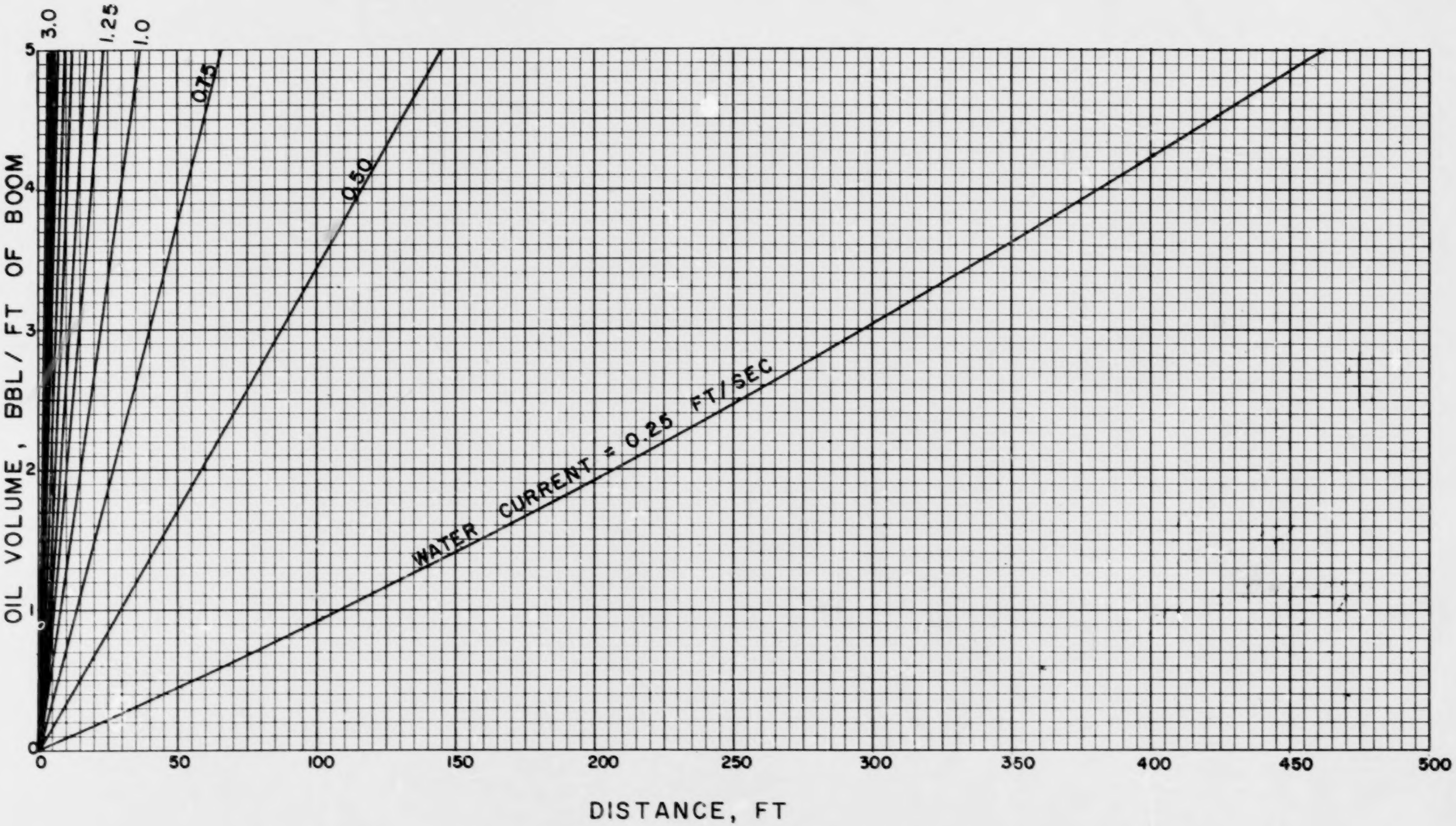


Figure 16. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.98, μ = 23,520 cp.

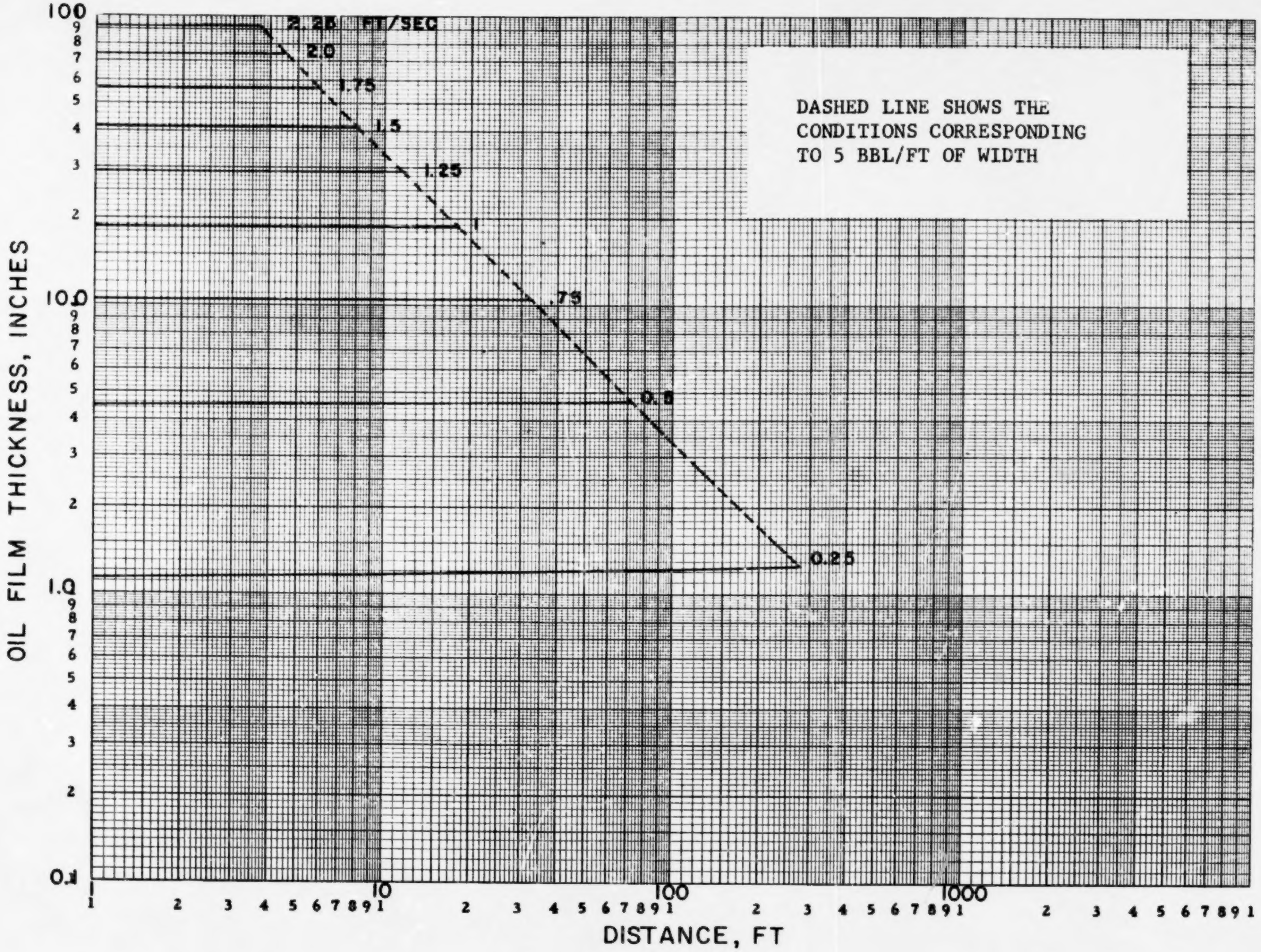


Figure 17. Oil film thickness versus distance for various water current speeds for oil with sp. gr. = 0.99, μ = 58,000 cp.

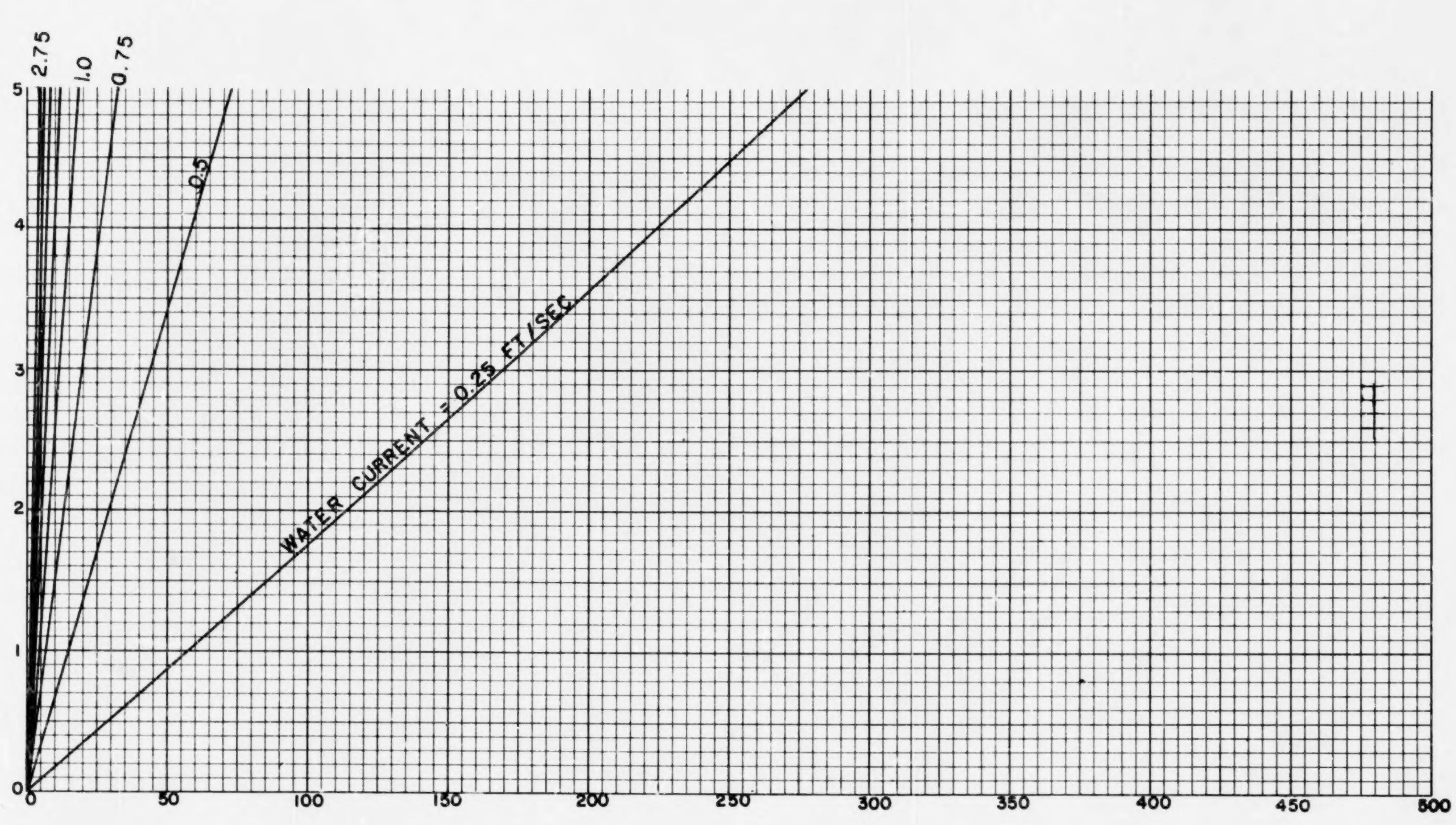


Figure 18. Cumulative oil film volume per unit width at various distances and water velocities for oil with sp. gr. = 0.99, μ = 58,000 cp.

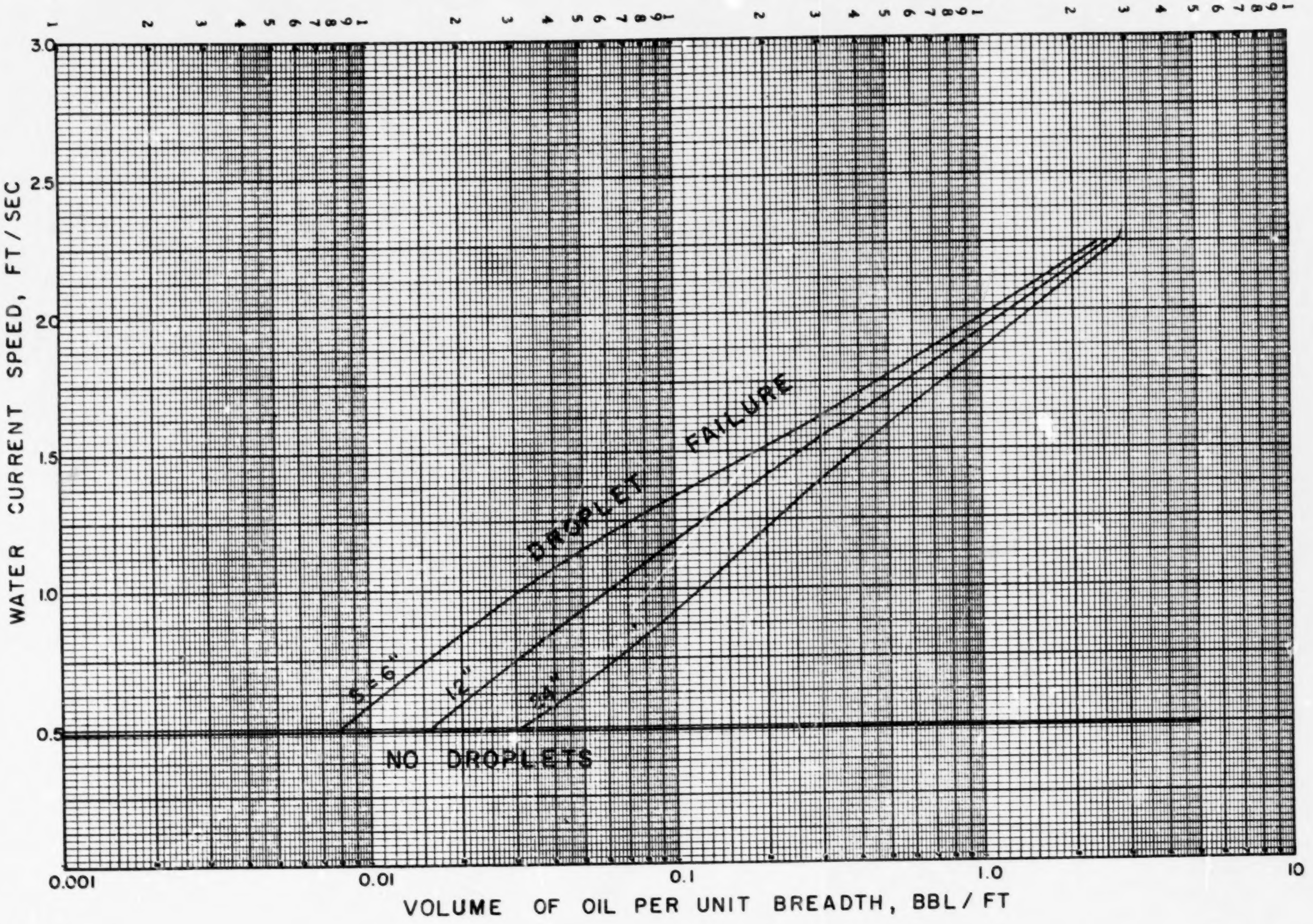


Figure 19. Failure diagram for oil with sp. gr. = 0.8, σ = 5 dynes/cm.

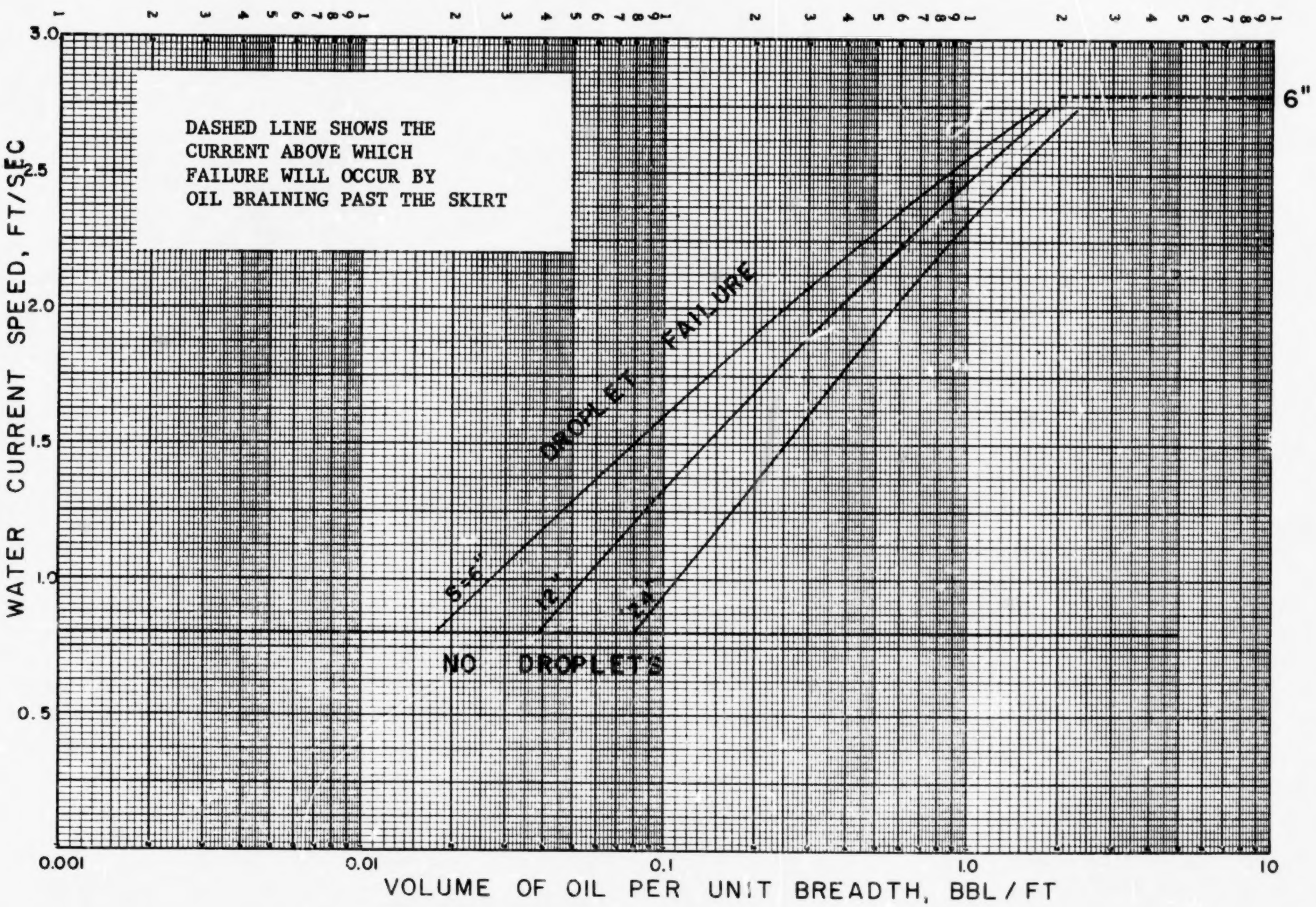


Figure 20. Failure diagram for oil with sp. gr. = 0.8, $\sigma = 40$ dynes/cm.

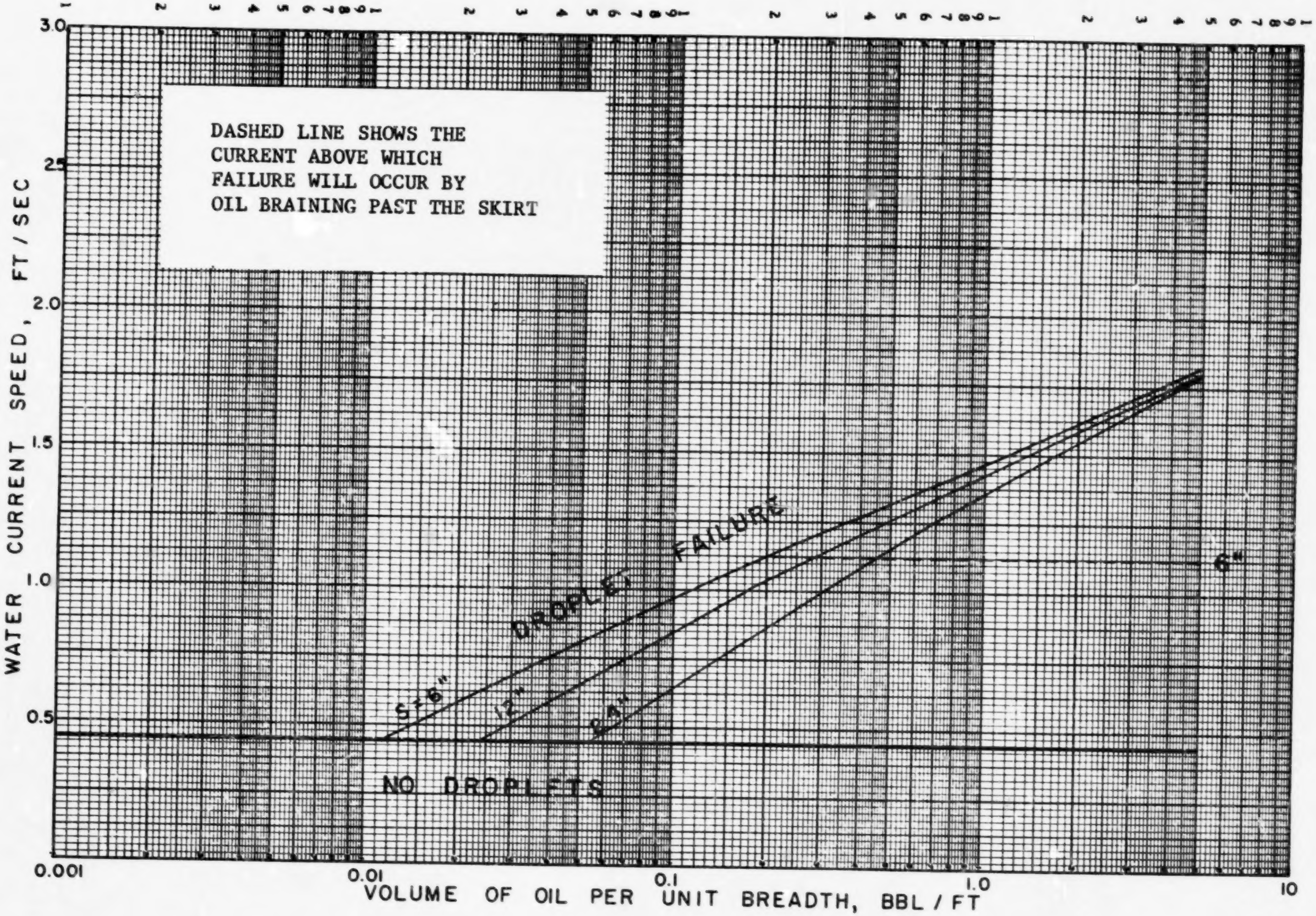


Figure 21. Failure diagram for oil with sp. gr. = 0.90, σ = 5 dynes/cm.

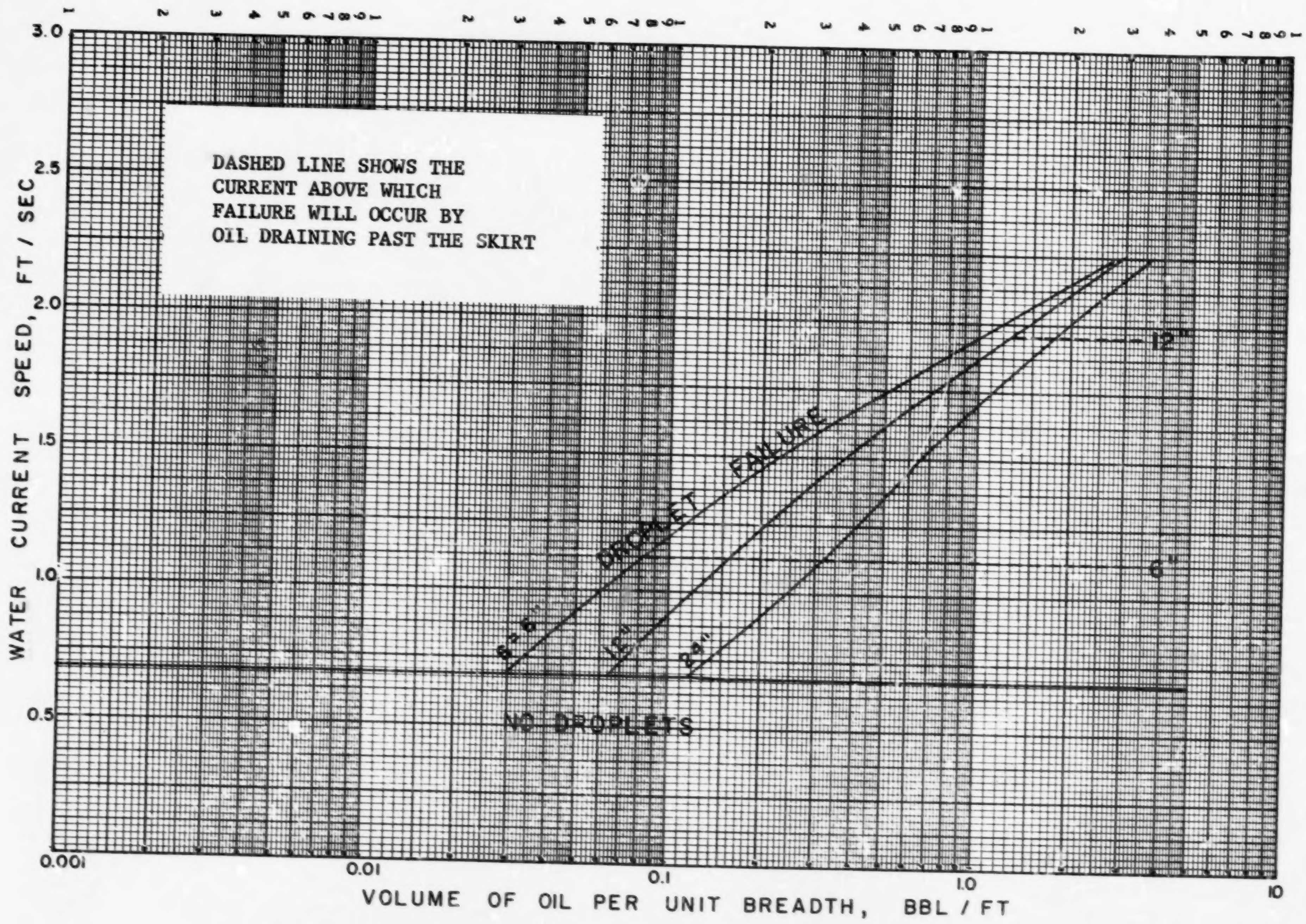


Figure 22. Failure diagram for oil with sp. gr. = 0.90, $\sigma = 40$ dynes/cm.

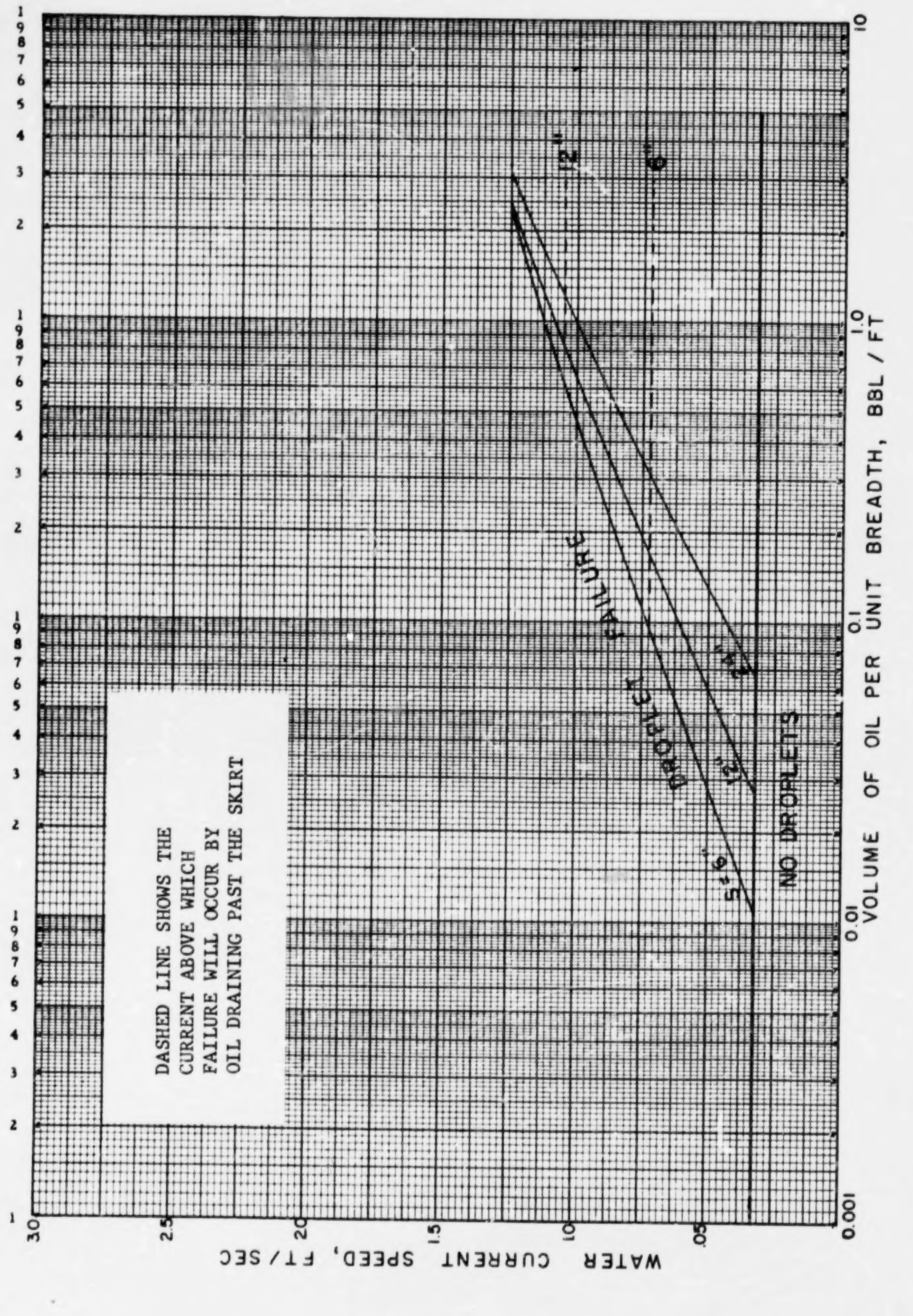


Figure 23. Failure diagram for oil with sp. gr. = 0.95, σ = 5 dynes/cm.

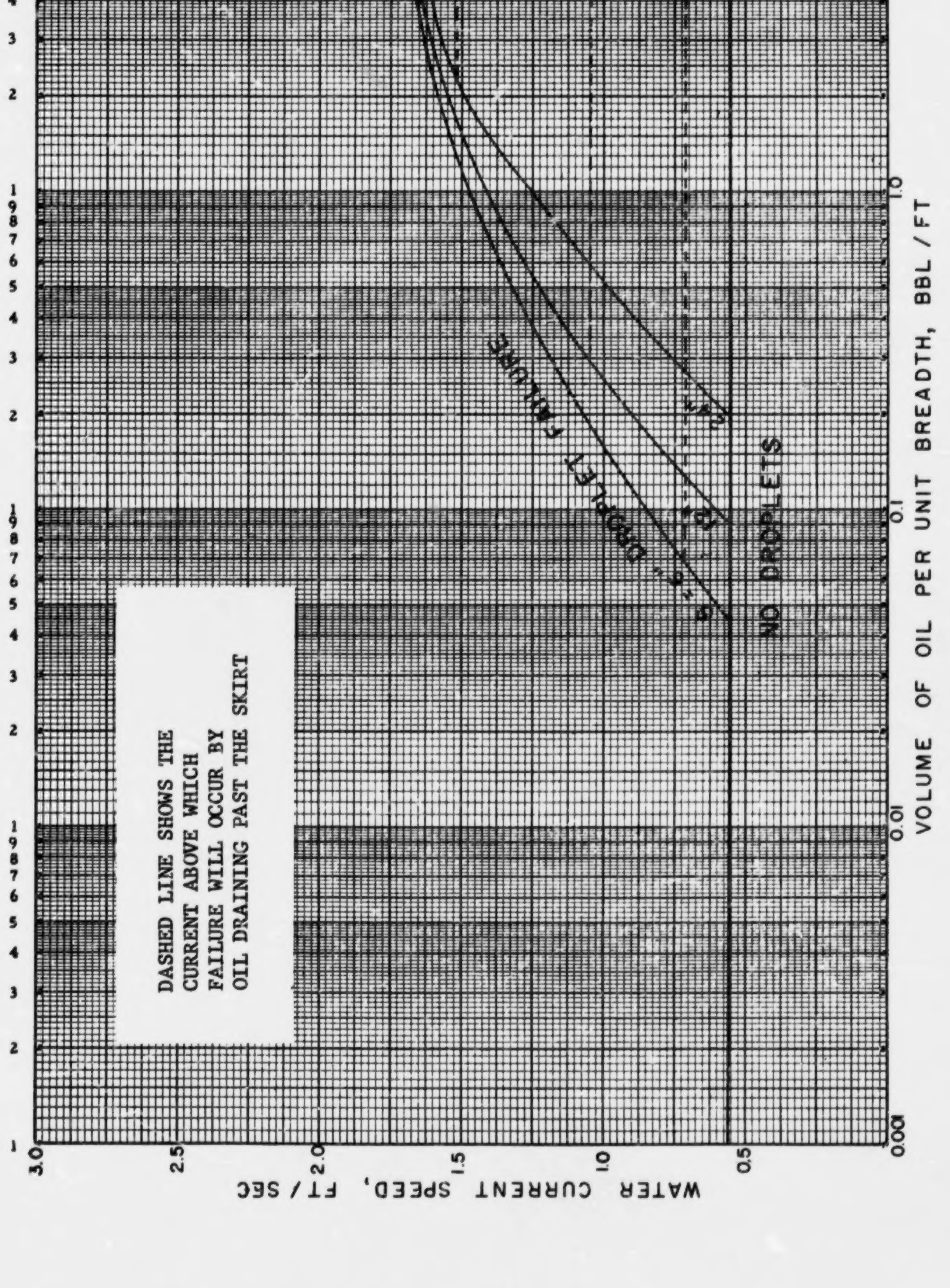
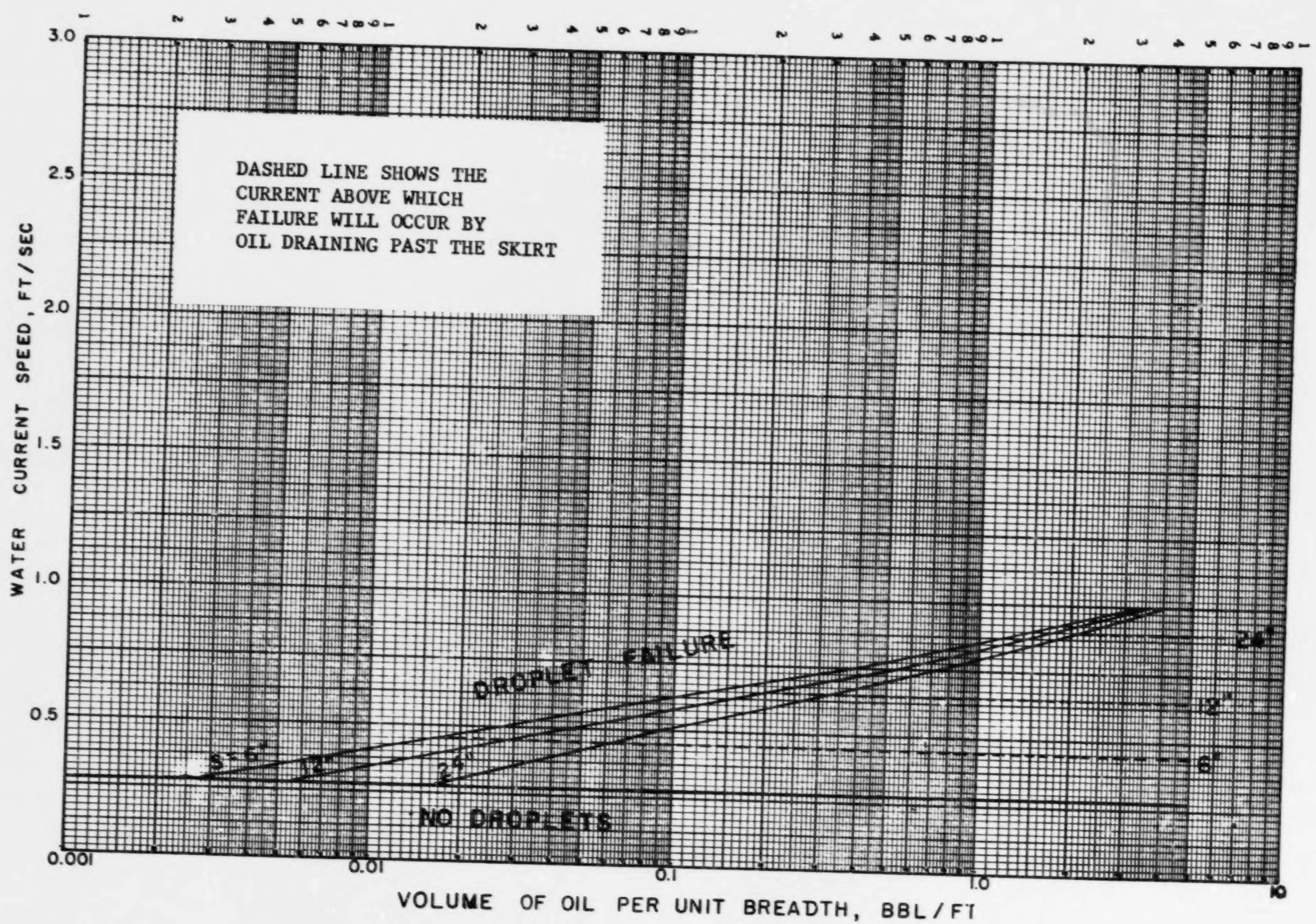


Figure 24. Failure diagram for oil with sp. gr. = 0.95, $\sigma = 40$ dynes/cm.



DASHED LINE SHOWS THE
CURRENT ABOVE WHICH
FAILURE WILL OCCUR BY
OIL DRAINING PAST THE SKIRT

Figure 25. Failure diagram for oil with sp. gr. = 0.98, $\sigma = 5$ dynes/cm.

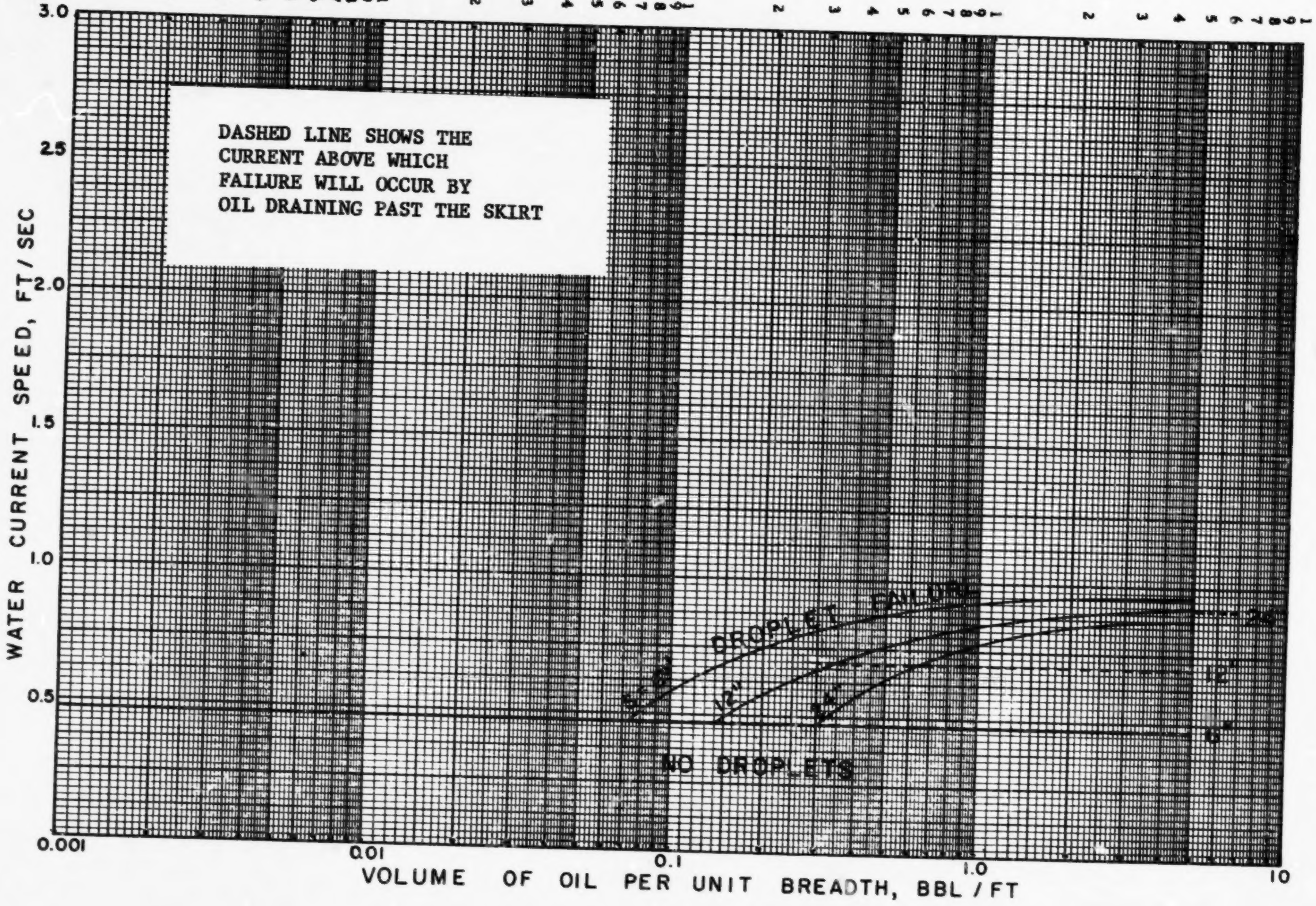


Figure 26. Failure diagram for oil with sp. gr. = 0.98, $\sigma = 40$ dynes/cm.

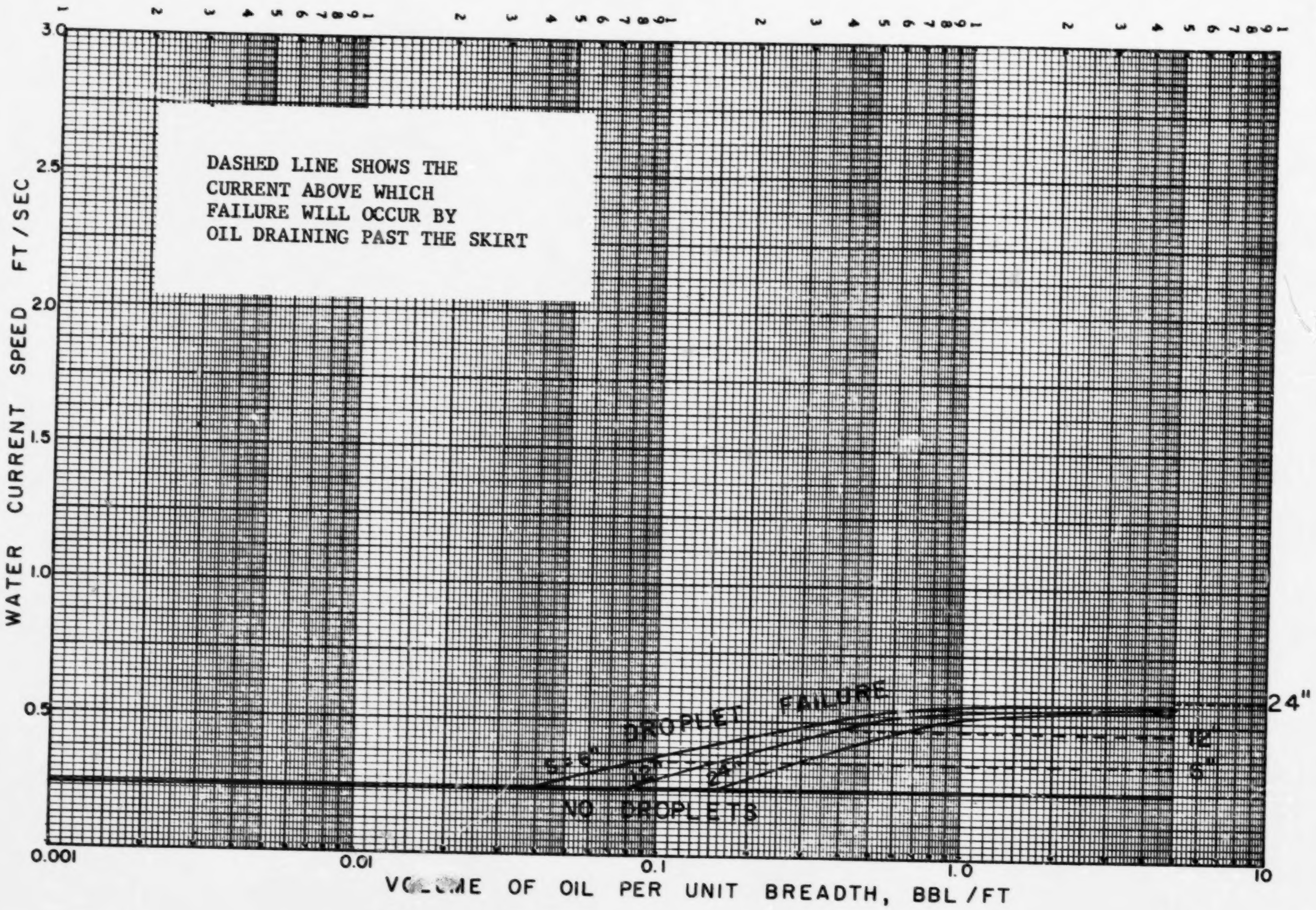


Figure 27. Failure diagram for oil with sp. gr. = 0.99, σ = 5 dynes/cm.

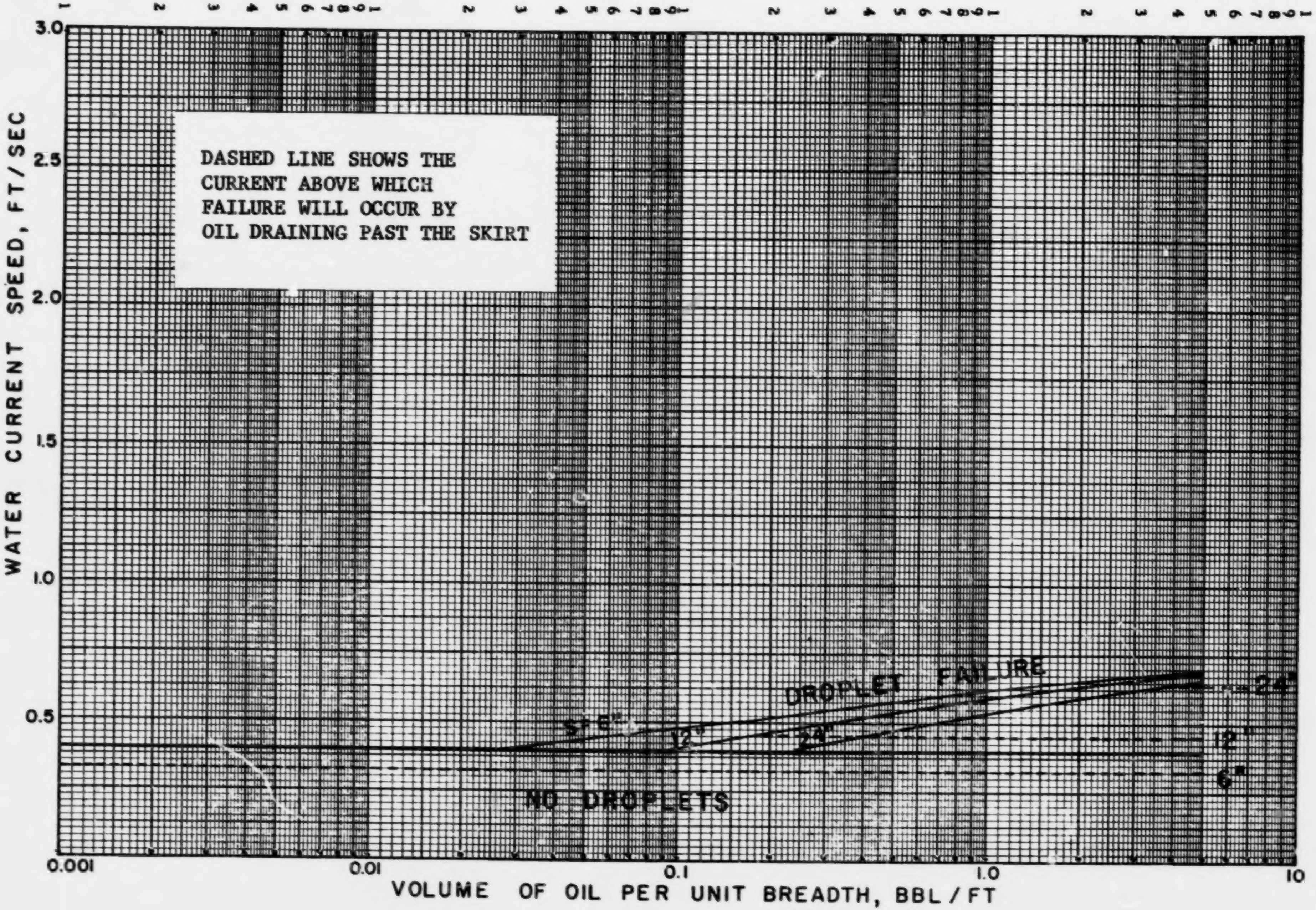


Figure 28. Failure diagram for oil with sp. gr. = 0.99, $\sigma = 40$ dynes/cm.

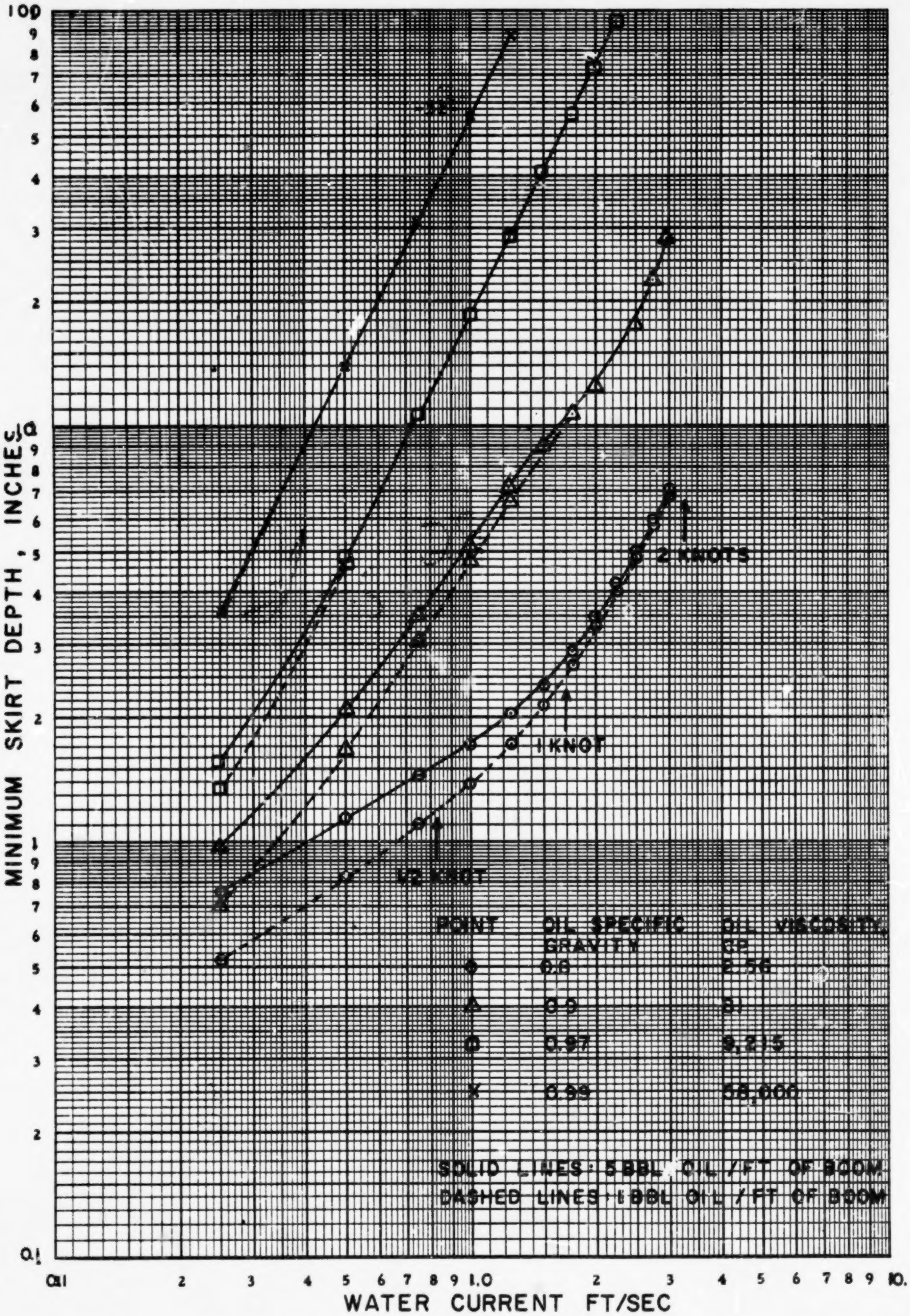


Figure 29. Minimum skirt depth to prevent draining.

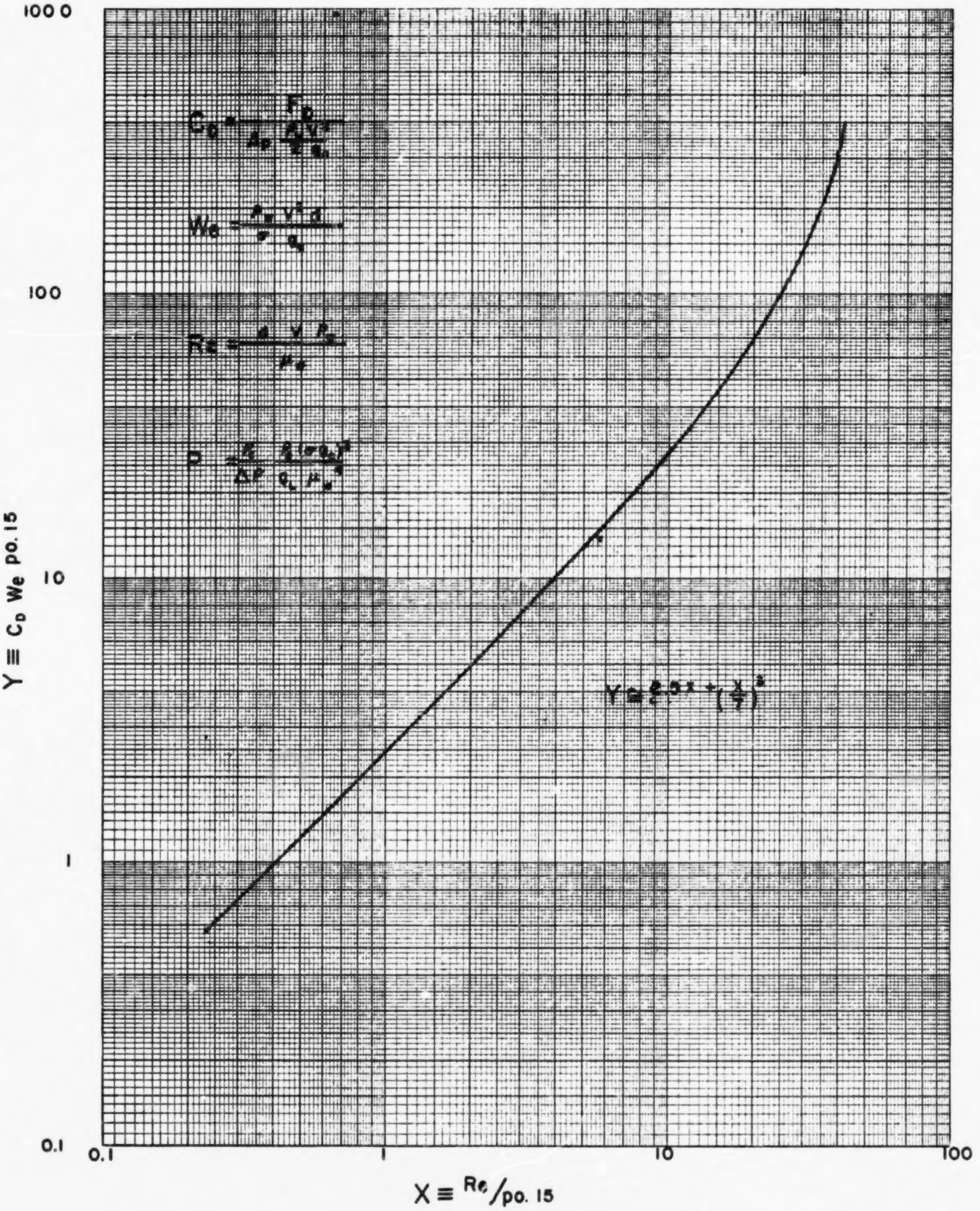


Figure 30. Hu & Kintner's correlation for the drag coefficient of droplets in liquid – liquid systems.

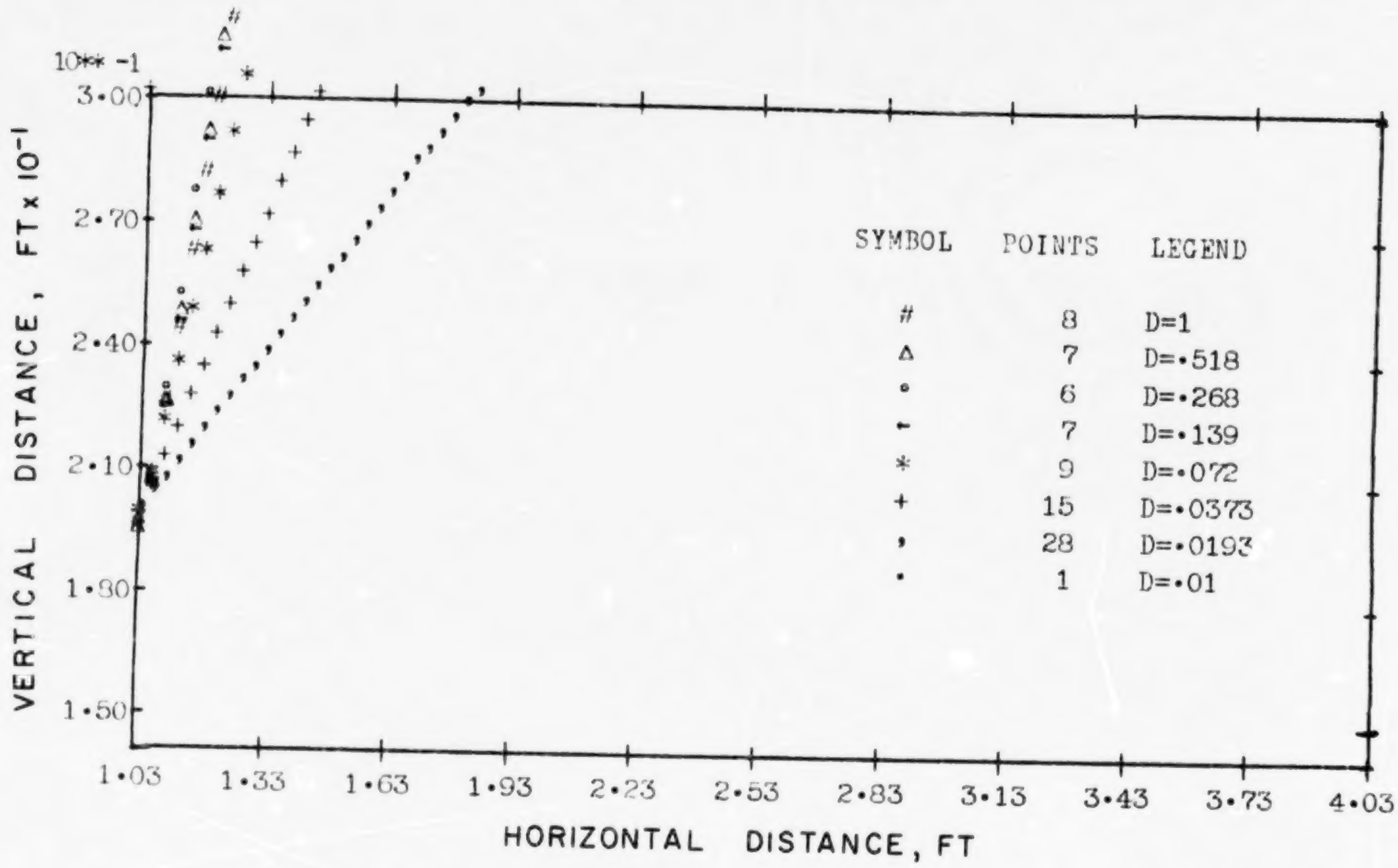


Figure 31. Trajectory of 0.80 sp. gr. oil drops (20 dynes/cm), in 0.5 ft/sec water current.

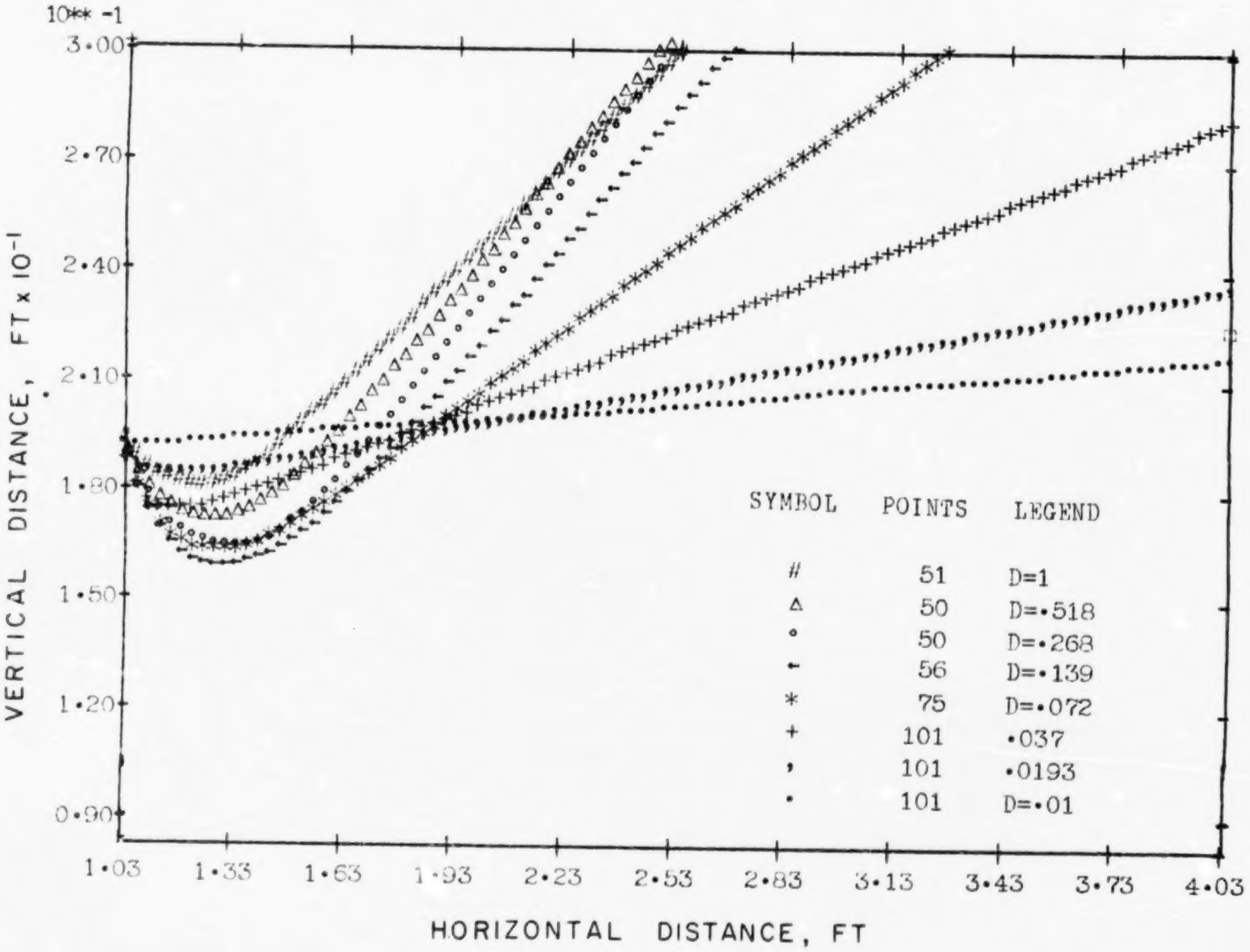


Figure 32. Trajectory of 0.80 sp. gr. oil drops (20 dynes/cm), in 3.0 ft/sec water current.

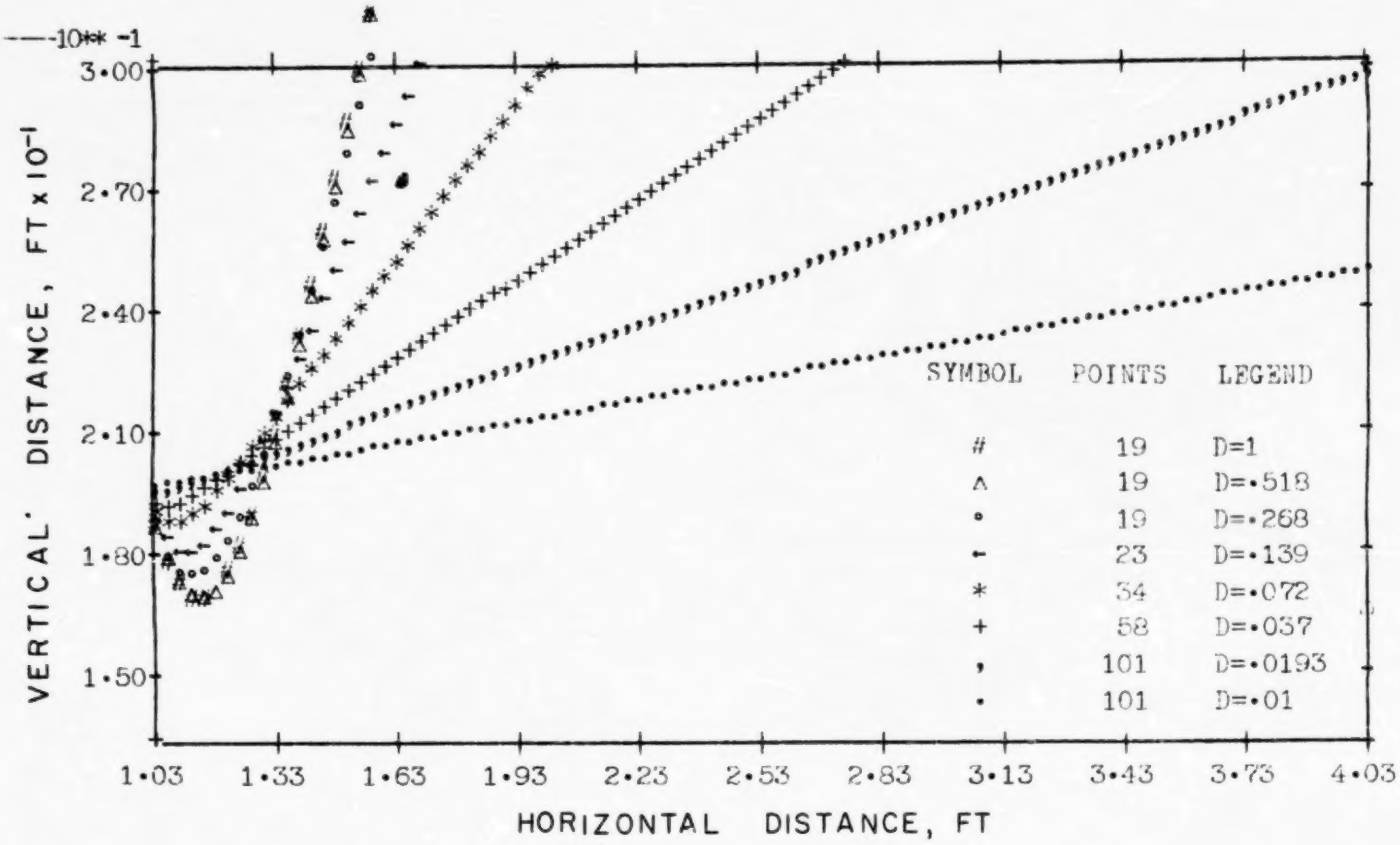


Figure 33. Trajectory of 0.97 sp. gr. oil drops (20 dynes/cm), in 0.5 ft/sec water current.

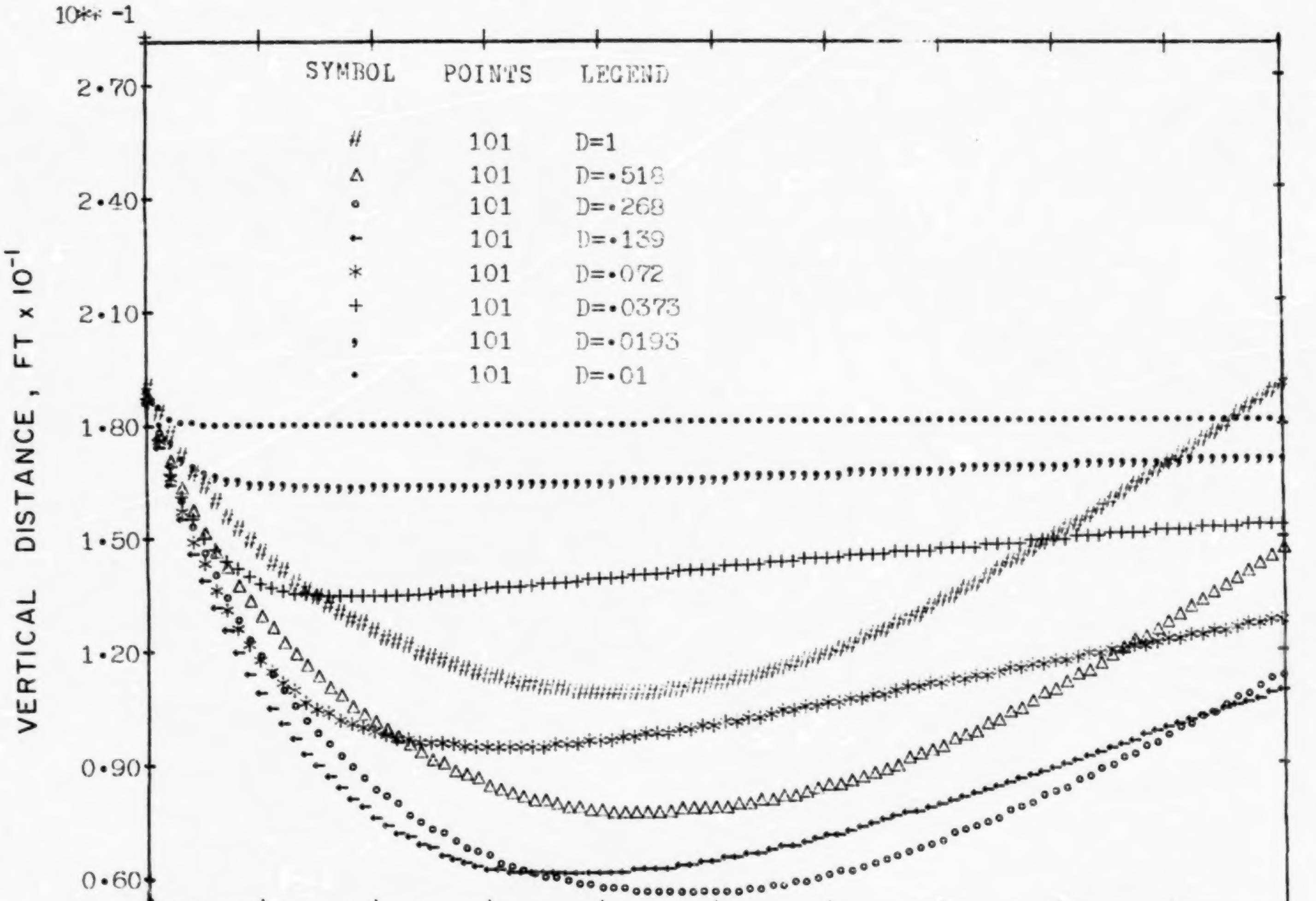


Figure 34. Trajectory of 0.97 sp. gr. oil drops (20 dynes/cm), in 3.0 ft/sec water current.

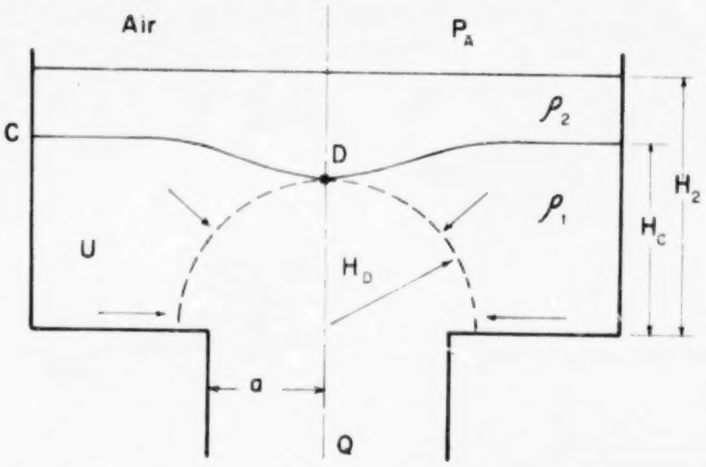


Figure 35. Geometry and definition of terms for the tank drainage problem.

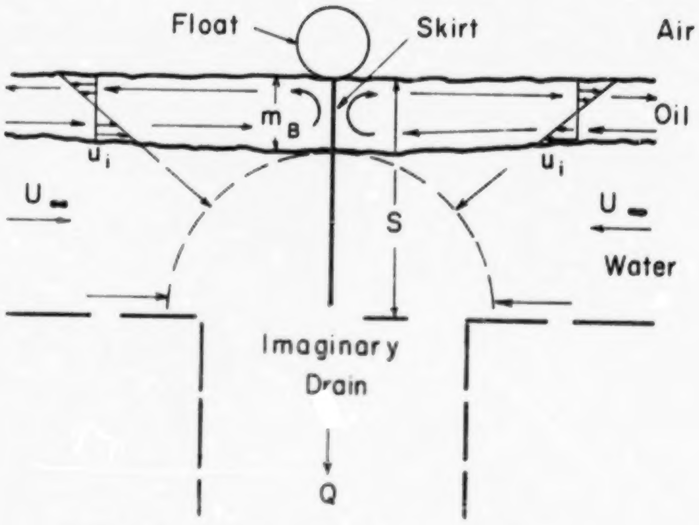


Figure 36. Re-interpretation of the original problem.

Order of magnitude analysis 12 shows that this simplication is possible so long as

$$\left(\frac{m_B}{L}\right)\left(\frac{m_B u_i \rho_o}{\mu_o}\right) \lesssim 1 \qquad (32)$$

where m_B is the oil thickness at the boom, L is the total length (x-direction) of the spill, u_i is the velocity at the oil-water interface and ρ_o and μ_o are the oil density and viscosity, respectively. Integrating (31) with the boundary condition

$$\text{at } y = m/2$$

$$\frac{\mu_o}{g_c}\left.\frac{\partial u}{\partial y}\right|_{m/2} = \tau_i$$

implies that the shear stress in the oil phase is constant:

$$\frac{\mu_o}{g_c}\frac{\partial u}{\partial y} = \tau_i \qquad (33)$$

Thus, the slope of the profile is constant, as shown by the solid line in the sketch above. It is clear that this is not entirely consistent with the known zero slope at the air-oil interface, but it is also evident that this need not cause a serious error in the calculated flow of oil.

Integrating (33) with the boundary condition

$$\text{at } y = 0$$

$$u = 0$$

gives the velocity profile in the oil:

$$u = \frac{\tau_i g_c}{\mu} y \qquad (34)$$

which, at the oil-water interface is

$$u_i = \frac{\tau_i g_c}{\mu}\,\frac{m}{2} \qquad (35)$$

Boundary Layer Equations

The drag caused by fluid flowing over the surface of a solid plate at zero angle of incidence has been well understood for many years. An excellent survey of this body of work is given in Reference 12. The equation relating the local surface shear stress τ to the free-stream flow velocity U_∞ is

$$\tau = \frac{\rho_w (U_\infty)^2}{2 g_c}\, C_F' \qquad (36)$$

where ρ_w is the water density and C_F' is friction factor, or drag coefficient, which depends on the Reynolds number R

$$C_F' = \phi(R)$$
$$R = \frac{x\, U_\infty \rho_w}{\mu_w} \qquad (37)$$

Since C'_F varies with x, note that τ does, also. Equations for C_F' are shown below.

An important difference between the flat plate and the oil interface is the fact that the interface is moving. If the plate were moving at velocity u_i one would simply use the relative velocity U_∞ - u_i instead of U_∞. This modification will be introduced without other direct justification into (36) and (37).

$$\tau_i = \frac{\rho_w (U_\infty - u_i)^2}{2 g_c} \qquad (38)$$

where

$$C_F' = \phi\left(\frac{x\,(U_\infty - u_i)\,\rho_w}{\mu_w}\right) \qquad (39)$$

Schlichting[12] present equations for C'_F as follows, depending on

$$R = \frac{x(U_\infty - u_i)\rho_w}{\mu_w}$$

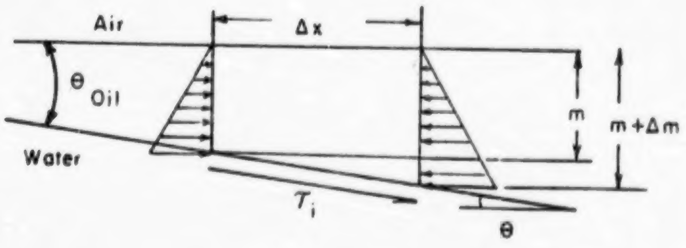
$$C_F' = 0.664/\sqrt{\bar{R}} \tag{40}$$

$$C_F' = [2 \log_{10} R - 0.65]^{-2.3} \tag{41}$$

The criterion of which to use when, is not entirely clear. Some data indicate that (40) applies until $R - 10^7$ while others show that (41) applies down to 3 x 10^5. For purposes of the present analysis (41) will be used uniformly, since most cases of interest are in the range $R > 3 \times 10^5$. As an added justification for this decision, it is known that if pressure increases in the flow direction, as it will in this case, the transition from a laminar (40) to a turbulent (41) boundary layer occurs sooner.

Force Balance

Another mathematical relationship can be derived by using the fact that the oil is "piled-up" by the water. Considering the sketch below



a force balance in the x-direction shows that

$$\tau_i = \rho_o \frac{g_L}{g_c} m \frac{\Delta m}{\Delta x} \tag{42}$$

The interfacial shear stress must thus be balanced by the film thickness gradient.

Calculation Procedure

Extraction of the oil film thickness as a function of distance from equations (35), (38), and (42) involves trial-and-error procedures as follows:

1. Set distance x
2. Assume m
3. Calculate $\Delta m/\Delta x$
4. Obtain u_i by trial-and-error simultaneous solution of the substituted relationship:

$$\sqrt{2\mu_o\rho_o \frac{g_L}{g_c^2}\left(\frac{\Delta m}{\Delta x}\right)u_i}$$

$$= \frac{\rho_w (U_\infty - U_i)^2}{2g_c} \; C_F' \left(\frac{x(U_\infty - U_i)\rho_w}{\mu_w}\right)$$

5. Check the assumed m's agreement with

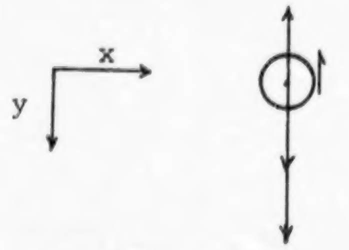
$$\frac{\tau_i}{\rho_o \frac{g_L}{g_c} \frac{\Delta m}{\Delta x}}$$

from (42) and repeat if they do not agree.
6. Set x at the next incremental distance and repeat until all of the spilled oil has been accumulated. This then fixes L and $m(x)$ for $0 < x < L$.

The computer program listing is shown on the following pages. The results were already presented in Figures 5 to 18.

APPENDIX 2
MOTION OF OIL DROPLETS UNDER THE SLICK

An oil droplet entrained in the water flowing under an oil slick experiences the following forces: The implicit assumption of uncoupling the x- and y-direction motions of the drop is strictly justified only in the Stokes region.



B = buoyant force

D = drag force

G = gravity force

S = sidewise force

The buoyant and gravity forces are simply

$$B = \frac{\pi}{6} d^3 \rho_w \frac{g_L}{g_c} \tag{43}$$

$$G = \frac{\pi}{6} d^3 \rho_o \frac{g_L}{g_c} \tag{44}$$

The Drag Force

The drag force can be written in terms of a drag coefficient C_D:

$$D = C_D \frac{\pi}{4} d^2 \frac{\rho_w (v_P - v_F) |(v_P - v_F)|}{2g_c} \tag{45}$$

For a solid sphere, the drag coefficient for non-accelerating motion depends on Reynolds number Re, only, where

$$Re \equiv \frac{d|v_P - v_F|\rho_w}{\mu_w} \tag{46}$$

For a liquid particle, however, the dependence is more complex because of

1. deformation of the droplet from spherical shape
2. oscillation of the droplet shape about some near-spherical average shape
3. circulation within the droplet caused by shear stresses induced at the surface of the drop

Hu and Kintner,[19] reporting on an extensive set of experiments with various immiscible liquid systems, found that their data could be correlated with Reynolds number and two additional dimensionless groups, the Weber number

$$We \equiv \frac{d\,|(v_P - v_F)|^2\,\rho_w}{\sigma\, g_c} \tag{47}$$

and a fluid property grouping,

$$P = \left(\frac{\rho_w}{\rho_w - \rho_o}\right)\left(\frac{\rho_w\,(\sigma\, g_c)^3}{g_L\,\mu_w^4}\right) \tag{48}$$

Their correlation is shown in Figure 30. The approximating equation shown on the figure will be very useful in calculating terminal velocities, as discussed below. While this correlation was found to describe Hu and Kintner's results very well and will, indeed, be used here, it must be regarded with some caution since it does not extrapolate properly to the Stokes formula

$$C_D = 24/\mathrm{Re} \tag{49}$$

as the surface tension and droplet viscosity become very large, approximating a solid sphere; also, it does not contain the droplet viscosity.

The transverse component of the boundary layer flow in Region II is given in Schlichting's book[12] for laminar boundary layers:

$$\frac{v_F}{U_\infty} = \frac{0.865}{\left(\dfrac{x\,U_\infty\,\rho_w}{\mu_w}\right)^{1/2}}\;\frac{y}{\delta} \tag{50}$$

No expression was found for the turbulent boundary layer case, but it is not difficult to derive one:

1. The continuity equation for an incompressible flow is

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{51}$$

2. Knowing $u(x,y)$, v can be determined:

$$v(x,\,y) = -\int_0^y \left(\frac{\partial u\;(x,\,y)}{\partial x}\right) dy \tag{52}$$

3. Schlichting gives

$$u = U_\infty \left(\frac{y}{\delta}\right)^{1/7} \tag{53}$$

and

$$\delta = 0.37 \left(\frac{x\,U_\infty\,\rho_w}{\mu_w}\right)^{-1/5} x \tag{54}$$

4. Substitution into (52) above yields

$$\frac{v_F}{U_\infty} = \frac{0.037}{\left(\dfrac{x\,U_\infty\,\rho_w}{\mu_w}\right)^{1/5}} \left(\frac{y}{\delta}\right)^{8/7} \tag{55}$$

The Sidewise Force

The sidewise force S is not as well understood as the drag force. There seems to be agreement that a particle in a velocity profile flow experiences a sidewise force in the direction of increasing velocity. (In our case of an oil droplet, the force would act downward.) There is some difference of opinion, however, as to the way S should be determined, as evidenced in references 23 and 24.

Theodore[25] measured S for non-rotating, non-translating spheres held at various radial positions in a tube. He correlated his data with the following equation

$$S = \frac{4.41}{g_c}\;\rho_w\, d^3\;\Delta u\;\frac{\partial u}{\partial y}\left(1 - 3\,\frac{d}{R_t}\right) \tag{56}$$

where R_t is the tube radius, and Δu is the relative velocity past the particle. For a moving particle, Brenner[26] found that a particle in a shear field lags behind the local fluid velocity with a velocity difference in laminar flow of

$$\Delta u = u_{max}\left(\frac{1}{12}\;\frac{d}{R_t}\right) \tag{57}$$

For the boundary layer flow case at hand,

$$u_{max} = U_\infty \tag{58}$$

$$R_t = \delta \tag{59}$$

where δ is the boundary layer thickness in the water. Substituting above,

$$S = \frac{0.735}{g_c}\;\rho_w\, d^4\;\frac{U_\infty}{\delta}\;\frac{\partial u}{\partial y}\left(1 - 3\,\frac{d}{\delta}\right) \tag{60}$$

Simplifications

Using the previous equation, the importance of S can be estimated in comparison with the net buoyant force. For U_∞ of one foot/sec with ρ_w = 62.4 lb/ft^3 and μ_w = 1 cp, the table below shows δ, the boundary layer thickness calculated from equation (54):

x Ft	δ Ft
1	0.0376
10	0.238
30	0.572
100	1.51
300	3.61

Similarly, calculations can be made for $\frac{\partial u}{\partial u}$ by differentiating (53):

$$\frac{\partial u}{\partial y} = \frac{1}{7}\;\frac{u}{y} \qquad (61)$$

In comparing S with the net buoyant force, the magnitudes

$$S' \equiv \frac{1.402}{g_L}\;\frac{d}{\delta}\;\frac{\rho_w}{\rho_o}\;U_\infty\;\frac{\partial u}{\partial y}\left(1 - 3\,\frac{d}{\delta}\right)$$

$$\text{and } NBF \equiv \frac{\rho_w}{\rho_o} - 1$$

are compared, respectively. For ½-inch drops of 0.93 specific gravity oil, at $y = \delta/2$ for $x = 30$ ft

$$S' = 0.00121$$

$$NBF = 0.075$$

and for other conditions, order of magnitude analysis shows, that since

$$\frac{\partial u}{\partial y} = O\;\frac{U_\infty}{\delta}$$

and $d \simeq \frac{.02}{U_\infty^2}$ from equation 3,

$$S' \simeq \frac{1}{30}\;\frac{.02}{U^2\delta}\;U_\infty\;\frac{U_\infty}{\delta} \qquad (62)$$

$$\simeq \frac{.0007}{\delta^2}$$

Since δ increases with x, and S' is less than 2% of NBF at the conditions above, it becomes even smaller with increasing x and will be neglected in this analysis.

Equations (50) and (55) similarly can be used to show that v_F should be small compared with v_t over most conditions. At $Re = 10^6$, equation (55) predicts $v_F = 0.0023\ U_\infty$ at the edge of the boundary layer. Making calculations of v_t, to be discussed below, for the drop sizes predicted by equation (3), the terminal velocities are as low as 0.01 ft/sec only for very low values of interfacial tension (5 dynes per centimeter), large oil densities (0.95 and above), and high water current velocities (over 2.5 ft/sec). For the present, v_F will be neglected.

The Transient Period

The sum of the forces acting on a typical drop is equal to its mass plus its "virtual mass," derived in reference 17 for example, times its acceleration:

$$G - B - D = \frac{1}{g_c}\,(m + m_V)\;\frac{d\,v_P}{dt} \qquad (63)$$

$$1 - \frac{\rho_w}{\rho_o} - \frac{3}{4}\;\frac{C_D}{g_L d}\;\frac{\rho_w}{\rho_o}\;v_P\,|v_P|$$

$$= \frac{U_\infty}{g_L}\left(1 + \frac{\rho_w}{2\rho_o}\right)\left(\frac{d\,v_P}{dx}\right) \qquad (64)$$

Given the initial velocity and position of the oil droplet, the above equation can be solved to determine the velocity of the particle at any subsequent position. The integral of the particle velocity then gives its vertial position at any subsequent time, or equivalently, at any downstream distance.

As the drop is torn off the head wave, it receives a downward component of velocity from the partially deflected water flow. It is important to establish the depth of penetration of the oil droplet into the water since this might affect the total rise time significantly.

Equation (64) above is a non-linear first order, ordinary differential equation of a form suitable for numerical solution by the Runge-Kutta method. A computer program was written employing this method, and it is shown in the attached listing. The results of some calculations made with the program are shown on the plots in Figures 31 to 34. The initial downward velocity was chosen as $U_\infty/2$. For the cases studied the following trends are clear:

1. higher density droplets penetrate farther into the water
2. at a given water velocity, there exists a certain size drop which penetrates deeper than larger or smaller sizes
3. higher water velocities cause deeper penetrations.

A somewhat surprising result of the calculations was the short distance required, even for the highest density and water velocity, to reach terminal rise velocity. Figure 34 shows a maximum of 4 feet is required for 0.268-inch oil drops of 0.97 specific gravity to reach terminal rise velocity; indeed, the maximum stable drop size for these conditions is 0.0208-inch according to equation (3). The negligible penetration of drops in this size range justifies ignoring the transient aspects of the droplet motion: the drops can, with practically no error, be assumed to start with no vertical velocity and achieve terminal speed instantaneously.

Calculation of Terminal Velocity

Setting the right side of (64) equal to zero in accordance with the preceeding arguments, the terminal velocity v_t is found by solving the equation

$$1 - \frac{\rho_w}{\rho_o} - \frac{3}{4}\;\frac{C_D}{g_L d}\;\frac{\rho_w}{\rho_o}\;v_t\,|v_t| = 0 \qquad (65)$$

with C_D given on Figure 30.

Substitution of the approximating equation for C_D along with the definitions of We and P from equations (47) and (48), leads to the following cubic after some algebraic manipulation:

$$|v_t|^3 + a\,|v_t| + b = 0 \qquad (66)$$

where

$$a = 858\left(\frac{P^{0.15}\,\mu_w}{\rho_w\,d}\right)^2 \qquad (67)$$

$$b = - \frac{28}{3}$$

$$\frac{p^{0.30} \; g_L \; d \left(1 - \frac{\rho_o}{\rho_w}\right) u_w}{\sigma \, g_c} \quad \left(\frac{7 P^{.15} \; \mu_w}{\rho_w \, d}\right)^2 \tag{68}$$

The one positive real root of (66) is for $\rho_o < \rho_w$.

$$v_t = A + B \tag{69}$$

where

$$A = \sqrt[3]{-\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}} \tag{70}$$

$$B = \sqrt[3]{-\frac{b}{2} - \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}} \tag{71}$$

Terminal velocities for various oil densitites and interfacial tensions were calculated as shown above. The program listing is shown, attached. The results are presented in Table 2 for interfacial tensions of 10, 20, 30 and 40 dynes/cm. The zeros in the table for large droplets of low density were included to indicate that the range of the C_D correlation was exceeded for those conditions.

APPENDIX 3. OIL LOSS BY DRAINING PAST THE BARRIER

Water flowing beneath the barrier causes a pressure reduction which could pull the oil under it. There is a clear need to understand the relation between oil properties and the flow conditions resulting in this kind of failure.

The Bathtub Problem - A Cognate Phenomenon

In draining a container of liquid from the bottom, it is well known that a dip or depression in the surface forms when the liquid depth reaches a certain critical height above the drain hole; this height depends on the size of the drain hole, as does the shape of the free surface. It is also well known that this dip grows downward very rapidly, eventually forming a vortex.

A recent paper[20] presents results of experiments on various liquids draining through several size holes from 1/8-inch to 1-inch diameter in 5-1/2 inch and 9-inch diameter cylinders. The height at which a dip formed was observed for both single liquid and two-immiscible-liquid cases. The latter observations are, of course, more interesting for possible application to flow of oil under a boom.

Observations[20] of the critical height at which a dip formed were adequately correlated with a remarkable simple mathematical model developed on the basis of the following assumptions:

1. The effects of viscosities of both lower and upper fluids are negligible.
2. The effect of surface tension at the interface of the lower and upper fluids is negligible.
3. The pressure at this interface is due to hydrostatic effects only.
4. At the instant prior to formation of the dip the flow is steady.
5. The initial depression or dip on the surface develops so rapidly as to reach into the drain instantaneously.

With the terms described in the sketch in Figure 35, the model developed in Reference 20 is evolved as follows:

1. The pressure at the interface is given by

$$P_i = \rho_2 \frac{g_L}{g_c} \Delta H + P_A \tag{72}$$

2. At the instant of formation of the dip, the volume flow rate Q into the drain is related to the assumed uniform velocity U and the height above the drain H_D by the following statement of the conservation of mass:

$$Q = 2\pi \; U H_D^2 \tag{73}$$

It is further assumed that U is uniform over the control volume indidated by the dashed line in Figure 35.

3. The Bernoulli equation for a streamline just below the interface is

$$P_c + \rho_1 \frac{g_L}{g_c} = H_c = P_D + \rho_1 \frac{g_L}{g_c} H_D + 1/2 \rho_1 U^2 \tag{74}$$

Combination of the above relations leads to the equation

$$H_c = H_D + \frac{Q^2}{8\pi^2 \left(1 - \frac{\rho_2}{\rho_1}\right) g_L \, H_D^4} \tag{75}$$

At the instant of formation of the dip.

$$\frac{dH_c/dt}{dH_d/dt} \cong 0 \tag{76}$$

in accordance with assumption 5. above. Use of this relationship gives the value of H at which a dip forms:

$$H = 0.55 \left[\frac{Q^2}{1 - \frac{\rho_2}{\rho_1} g_L}\right]^{1/5} \tag{77}$$

Considerations for the Present Problem

In attempting to apply the above type of approach to the problem of oil flow under a boom one fundamental assumption is implicit: the mechanism by which such flow actually occurs is the same as that for the draining problem. In other words, this approach assumes that failure of the boom occurs as a result of the action of hydrostatic, gravitational, and inertial forces, with negligible contribution from interfacial shear stress.

The analysis presented for draining a tank must be modified in several respects. Items of contrast in the two problems are summarized in Table 3. These will be treated in order.

TABLE 3. ASPECTS OF CONTRAST TO BE RESOLVED

Item	Tank Draining Problem	Oil Flow Under a Boom
1	Radial flow toward the drain hole	Two-dimensional flow toward and under the boom
2	Unrestrained flow toward the drain	Flow blocked by the boom
3	Finite volume of both fluids	Semi-infinite volume of the water phase
4	No lateral flow of either fluid except that into drain	Net flow of the water phase horizontally, and an imposed velocity at the oil water interface

1. The two-dimensional formulation of the drainage problem yields the same Bernoulli equation:

$$P_c + \rho_1 \frac{g_L}{g_c} H_c = P_D + \rho_1 \frac{g_L}{g_c} H_D + \frac{1}{2g_c} \rho_1 U^2 \qquad (78)$$

   where, now U is related to Q by

$$Q = U \times H_D \times B \qquad (79)$$

   and B is the unit length of the boom.

2. The presence of the boom skirt has no effect on the two-dimensional draining problem since it is located in a plane of symmetry. Now, the original problem will be changed slightly to symmetrical flow of water toward the boom from both sides, as illustrated in Figure 36. The implicit assumption, again, is that the oil will be entrained by the water in the flow field of Figure 36 in the same way that it is in the real-world problem of interest.

3. The imaginary boundary shown by the heavy dashed line in Figure 36 is introduced to resolve item number 3 of Table 3. This is arbitrary but admissible since, essentially, potential flow has been assumed in the water phase, anyway. The vertical location of the imaginary plane is taken to be the horizontal plane through the bottom of the skirt; this is the point where the streamlines of the water flow become parallel to the axis of the drain.

4. Item 4 of Table 3 is largely already resolved by the symmetry-of-flow assumption in Item 2 above. Since the oil phase is moving, however, the interfacial velocity will be subtracted from the water speed U_∞:

$$U = U_\infty \; u_i \qquad (80)$$

Results

Using equations (79), (78), and (76) the two-dimensional version of (77) is

$$H = 0.466 \left[\frac{Q^2}{\left(1 - \frac{\rho_2}{\rho_1}\right) g_L B^2} \right]^{1/3} \qquad (81)$$

Introducing U from (79), substituting for U from (80) and using

$$H = S - m_B \qquad (82)$$

the resulting equation for the minimum skirt length S required to prevent flow of oil under the boom is:

$$S = m_B + \frac{(U_\infty - u_i)^2}{g_L \left(1 - \frac{\rho_{oil}}{\rho_w}\right)} \qquad (83)$$

Input values of m_B and u_i for equation (83) were obtained from the Appendix 1 analysis for oil spill thickness distribution. The results of the calculations were presented earlier in Figure 29.

APPENDIX 4. COMPUTER PROGRAM LISTINGS

1. Boundary Layer Region Analysis

```
   REAL MG,M,MUO,MUW,MNMINUS1,MJ,MC,MJMINUS1,MJPLUS1,MN
10 DISPLAY " "
   DISPLAY " "
   DISPLAY " "
   JJ=0
   DISPLAY"*******************************************************"
   DISPLAY"* TYPE INPUT DATA AS FØLLOWS:"
   DISPLAY"* WATER CURRENT SPEED,FT/SEC ",#
   ACCEPT UINF
   DISPLAY"* WATER SPECIFIC GRAVITY: ",#
   ACCEPT PW
   DISPLAY"* WATER VISCOSITY,CP: ",#
   ACCEPT MUW
   DISPLAY"* OIL SPILL VOLUME/FT OF BOOM LENGTH, BBLS/FT: ",#
   ACCEPT QO
   DISPLAY"* OIL SPECIFIC GRAVITY : ",#
   ACCEPT PO
   DISPLAY"* OIL VISCOSITY, CP: ",#
   ACCEPT MUO
   DISPLAY"* LENGTH INCREMENT, FEET: ",#
   ACCEPT DX
   DISPLAY"*******************************************************"
   WRITE (1,901)
   PW=PW*62.4
   MUW=MUW*6.73E-04
   QO=QO*5.61
   PO=PO*62.4
   MUO=MUO*6.73E-04
   C1=(2.*MUO*PO)/32.2
   C2=(PW/2.)/32.2
   C3=PW/MUW
   XNMINUS1=0
   UNMINUS1=UINF/2.
   MG=((UINF↑2)/(64.4*((PW/PO)-1.)))
   IF (UINF.LE.1.0),DMNMINUS1=.01
   IF (UINF.GT.1.0.AND.UINF.LE.1.5),DMNMINUS1=.001
   IF (UINF.GT.1.5.AND.UINF.LE.2.0),DMNMINUS1=.0001
   IF (UINF.GT.2.0.AND.UINF.LE.2.25),DMNMINUS1=.00001
   IF (UINF.GT.2.25.AND.UINF.LE.2.50),DMNMINUS1=.000001
   IF (UINF.GT.2.50.AND.UINF.LE.2.75),DMNMINUS1=.0000001
   IF (UINF.GT.2.75.AND.UINF.LE.3.00),DMNMINUS1=.00000001
   XG=50.*MG
   QG=XG*MG
   IF(QG.GE.QO) GO TO 15
   QNMINUS1=QG
   MNMINUS1=MG
   GO TO 20
15 QN=QG
   MN=MG
   TIL=0.
   UN=0.
   XN=XG
   GO TO 65
20 J=0
25 XN=XNMINUS1+DX
   MJ=MNMINUS1+DMNMINUS1
30 K=0
   S=(MJ-MNMINUS1)/DX
   UK=UNMINUS1
35 R=C3*XN*(UINF-UK)
   CF=(2.*ALOG10(R)-0.65)↑-2.3
   TIL=(C1*UK*S)↑.5
   TIR=C2*(UINF-UK)↑2.*CF
   EK=(TIL-TIR)/TIL
   IF(ABS(EK).LT.0.005) GO TO 40
   IF (K.EQ.0.0) GO TO 45
   UKPLUS1=UK-(EK)/((EK-EKMINUS1)/(UK-UKMINUS1))
   GO TO 46
```

```
  45 K=1
     UKPLUS1=(UK+UINF)/2.
     IF (EK.GT.0.0), UKPLUS1=UK/2.0
  46 EKMINUS1=EK
     UKMINUS1=UK
     UK=UKPLUS1
     IF (UK.GT.0.000001) GØ TØ 35
     UK=1.0E-06
     GØ TØ 35
  40 UN=UK
     MC=TIL/PØ/S
     FJ=(MC-MJ)/MC
     IF (ABS(FJ).LT.0.01) GØ TØ 50
     IF (J.EQ.0.0) GØ TØ 55
     MJPLUS1=MJ-((FJ)/((FJ-FJMINUS1)/(MJ-MJMINUS1)))
     GØ TØ 60
  55 J=1
     MJPLUS1=MC
  60 FJMINUS1=FJ
     MJMINUS1=MJ
     MJ=MJPLUS1
     IF (MJ.GT.MNMINUS1) GØ TØ 30
     MJ=MNMINUS1*1.001
     GØ TØ 30
  50 MN=MJ
     QN=QNMINUS1+((MN+MNMINUS1)/2.)*DX
 901 FØRMAT (/5X,$X,FT$,2X,$M,IN.$,4X,$U,FT/SEC$,2X,$TAU,PSF$,
     5X,$Q,BBLS/FT$,3X,$SMIN$)
  65 M=MN*12.
     XP=XG+XN
     Q=QN/5.61
     JJ=JJ+1
     SMIN=MN+((UINF-UK)↑2/((32.2*(1.-(PØ/PW)))))
     SMIN=SMIN*12.
     WRITE (1,902) XP,M,UN,TIL,Q,SMIN
 902 FØRMAT (F9.3,F8.5,F10.6,F11.7,F9.4,F13.5)
     IF (QN.GE.QO),DISPLAY"NØ. ØF RØWS=",JJ
     IF (QN.GE.QO) GØ TØ 10
     DMNMINUS1=MN-MNMINUS1
     UNMINUS1=UN
     QNMINUS1=QN
     MNMINUS1=MN
     XNMINUS1=XN
     GØ TØ 20
1000 END
```

2. Runge Kutta Integration

```
   DIMENSION X(10),V(10)
   COMMON A,B,C,CS,U,SW,F
   REAL MUW,K1,K2,K3,K4
   GC=32.17
   GL=32.17
10 DISPLAY"INPUT DENSITY OF OIL(LB/FT3)** ",#
   ACCEPT RHO
   DISPLAY"INPUT SURFACE TENSION(LBF/FT)** ",#
   ACCEPT SIG
   DISPLAY"INPUT VISCOSITY OF WATER(CENTIPOISES)** ",#
   ACCEPT MUW
   MUW=MUW*6.73E-04
   DISPLAY"INPUT DENSITY OF WATER(LB/FT3)** ",#
   ACCEPT RHOW
   P=((RHOW/(RHOW-RHO))*(RHOW*(SIG*GC)**3)/(GL*(MUW**4)))**0.15
   AK=(1.-(RHOW/RHO))*(GL/(1.+(RHOW/(2.*RHO))))
   BK=(0.75*RHOW*SIG*GC*2.5)/((1.+(RHOW/(2.*RHO)))*RHO*P*P*MUW)
   CK1=(0.75*SIG*GC)
   CK2=(1.+(RHOW/(2.*RHO)))
   CK3=RHO*P
   CK4=(RHOW/(7.*P*MUW))**3.04
   CK=(CK1/(CK2*CK3))*CK4
   CS=MUW/RHOW
```

```
      DISPLAY"P= ",P
      DISPLAY"AK= ",AK
      DISPLAY"BK= ",BK
      DISPLAY"CK= ",CK
      NU=1
      U=4.
   20 A=AK/U
      OPEN (2,OUTPUT,//)
      ND=1
      D=1./12.
   30 DISPLAY"**************************************************"
      J=0
      DISPLAY""
      DISPLAY"ND=",ND
      DISPLAY"U=",U
      DISPLAY"D(IN)=",D*12.
      WRITE(1,900)
  900 FORMAT(//,3X,$X$,9X,$Y$,9X,$VP$,8X,$VF$)
      SW=1.0
      F=-1
      B=BK/(U*D)
      C=(CK/U)*(D)**1.04
      X(1)=1
      V(1)=U/2.
      H=.005
      N=1
      X0=1.
      V0=U/2.
      Y0=1.
   35 XZ=X0
      VZ=V0
      CALL RUNGEK(XZ,VZ,VF)
      K1=F*H
      XZ=X0+(H/2.)
      VZ=V0+(K1/2.)
      CALL RUNGEK(XZ,VZ,VF)
      K2=F*H
      XZ=X0+(H/2.)
      VZ=V0+(K2/2.)
      CALL RUNGEK(XZ,VZ,VF)
      K3=F*H
      XZ=X0+H
      VZ=V0+K3
      CALL RUNGEK(XZ,VZ,VF)
      K4=F*H
      DELV=1./6.*(K1+(2.*K2)+(2.*K3)+K4)
      X(N+1)=X(N)+H
      V(N+1)=V(N)+DELV
      IF (N-6)40,45,40
   40 X0=X(N+1)
      V0=V(N+1)
      N=N+1
      GO TO 35
   45 Y=Y0+(0.3*H)/U*(V(1)+V(3)+V(5)+V(7)+5*(V(2)+V(6))+6*V(4))
      Y1=1.2-Y
      WRITE (2,901) X(7),Y1
  901 FORMAT (2F10.6)
      J=J+1
      IF(Y.LE.0.9) GO TO 55
      IF(X(7).GE.4.0) GO TO 55
      IF (SW) 55,55,51
   51 Y0=Y
      X(1)=X(7)
      V(1)=V(7)
      X0=X(7)
      V0=V(7)
      N=1
      GO TO 35
```

```
55 IF (ND-8) 70,75,75
70 ND=ND+1
   D=D/1.93
   DISPLAY"NO. OF ROWS=",J
   GO TO 30
75 IF (NU-5) 90,10,10
90 NU=NU+1
   U=U-1.
   IF(U.LT.1.0),U=0.5
   CLOSE(2)
   DISPLAY"NO. OF ROW=",J
   GO TO 20
   END
   SUBROUTINE RUNGEK(X,V,VF)
   COMMON A,B,C,CS,U,SW,F
   REAL K
   R=(U*X)/CS
   IF (R-3.0E5) 10,10,20
10 K=0.085
   E=0.5
   GO TO 25
20 K=0.037
   E=0.2
25 VF=(K*U)/(R**E)
   IF (V-VF) 30,30,35
35 Z=-1.
   GO TO 40
30 Z=1.0
40 FOLD=F
   F=A+(Z*B*ABS(V-VF))+((Z*C)*ABS(V-VF)**3.04)
   IF ((F*FOLD).LE.0.0),SW=-1.
   RETURN
   END
```

3. Terminal Velocity Calculation

```
      DIMENSIØN RHØ(7),D(13),DLØG(13),VT(7,13)
      REAL MUW
      DATA RHØW,MUW,GL/62.4,.000673,32.17/
      DATA RHØ/.8,.85,.9,.95,.97,.98,.99/
      DATA D/.001,.002,.004,.0065,.01,.02,.04,.065,.1,.2,.4,.65,1./
      DØ 5 I=1,13
      D(I)=D(I)/12.
      DLØG(I)=ALØG10(D(I))
    5 CØNTINUE
      DISPLAY"INPUT SURFACE TENSIØN** ",#
      ACCEPT SIG
      ØPEN (2,ØUTPUT,//)
   10 DØ 20 I=1,7
      RHØ(I)=RHØ(I)*62.4
      P=((RHØW/(RHOW-RHØ(I)))*((RHØW*(SIG*GL)↑3)/(GL*(MUW↑4))))↑.15
      DØ 30 K=1,13
      A=2.5*(7.↑3)*((P*MUW)/(D(K)*RHØW))↑2
      B=(-28./3.)*((P*P*GL*D(K)*(1.-(RHØ(I)/RHØW))*MUW)/(SIG*GL))
      B=(B)*((7.*P*MUW)/(D(K)*RHØW))↑2
      AA=((-B/2.)+SQRT(((B↑2)/4.)+((A↑3)/27.)))↑.3333
      BB=-1.*ABS((-B/2.)-SQRT(((B↑2)/4.)+((A↑3)/27.)))↑.3333
      VT(I,K)=AA+BB
      R=(D(K)*VT(I,K)*RHØW)/MUW/P
      IF(R-40) 15,15,25
   25 VT(I,K)=0.0
      GØ TØ 30
   15 WRITE (2,90) DLØG(K),VT(I,K)
   30 CØNTINUE
   20 CØNTINUE
      DISPLAY"   D      .8       .85      .9       .95      .97
     .98      .99"
   90 FØRMAT(2F12.9)
      DØ 55 K=1,13
      D(K)=D(K)*12.
      WRITE(1,95)D(K),(VT(I,K),I=1,7)
   95 FØRMAT(F7.4,7F9.6)
   55 CØNTINUE
      CLØSE (2)
      END
```

Design Requirements For Booms

Commander W.E. Lehr, USCG
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Abstract

The general requirements for high seas oil spill cleanup equipment are detailed. Specific design considerations inherent to high seas boom development are also identified. In particular, the problems of oil retention capability and required barrier strength are discussed. The results, to date, of theoretical studies and tank model tests to provide fundamental engineering data for boom designers are reported. These studies provide information concerning the prediction of boom loads, shapes, and motions. A summary of current progress in the preliminary design of competing high seas barrier concepts is given.

At the present time, considerable thought and effort are being expended in developing equipment and procedures to prevent accidental spills of oil. These efforts include investigations into the feasibility of new tankship construction standards, development of improved navigation systems, provision of new and/or updated operating practices, and the design of oily water processing equipment, among others. When completed, they should result in a significant reduction in the size and number of chronic small scale spills which occur each year.

Unfortunately, experience shows that our best efforts cannot prevent the occasional occurence of major accidents at sea. Human error, mechanical failure, or environmental stress will continue to cause maritime disasters. Although relatively infrequent, accidents involving tankships and offshore oil production equipment may thus be expected to continue as sources for potential massive oil pollution incidents.

So long as the potential for massive oil spills exists, special techniques and equipment to facilitate spill cleanup in the coastal high-seas region will be required.

The Cleanup Process

Three specific steps are needed to provide a viable cleanup system. These are spill amelioration, containment and recovery.

Spill Amelioration. While not directly related to the cleanup problem, procedures and equipment to eliminate or reduce the size of a major oil spill is desirable. This is particularly true in tanker accidents. Some kind of emergency system that can be used to unload damaged cargo tanks, and thereby decrease the scope of follow-on cleanup efforts is needed.

Containment. Spilled oil will rapidly form a thin film over a wide region. This will occur through both natural spread phenomena and the influence of environmental action. Following Blokker, a nominal spill of 20,000 tons of crude oil may cover approximately 23½ square miles of ocean surface, to a thickness of 0.01 inches, eight hours after release.[1]

If spreading is allowed to occur, the efficiency of subsequent cleanup operations at sea is extremely doubtful. The efficacy of various mechanical recovery devices is severely reduced when required to deal with thin surface films. Additionally, the logistic and operating problems associated with the application of all cleanup techniques (chemical as well as mechanical) to large ocean surface areas are prohibitive. The need to confine spilled oil to a small area in relatively thick films as quickly as possible is a practical necessity. Thus, development of high seas barrier equipment is of primary importance.

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[1] Superior numbers refer to literature references at conclusion of text.

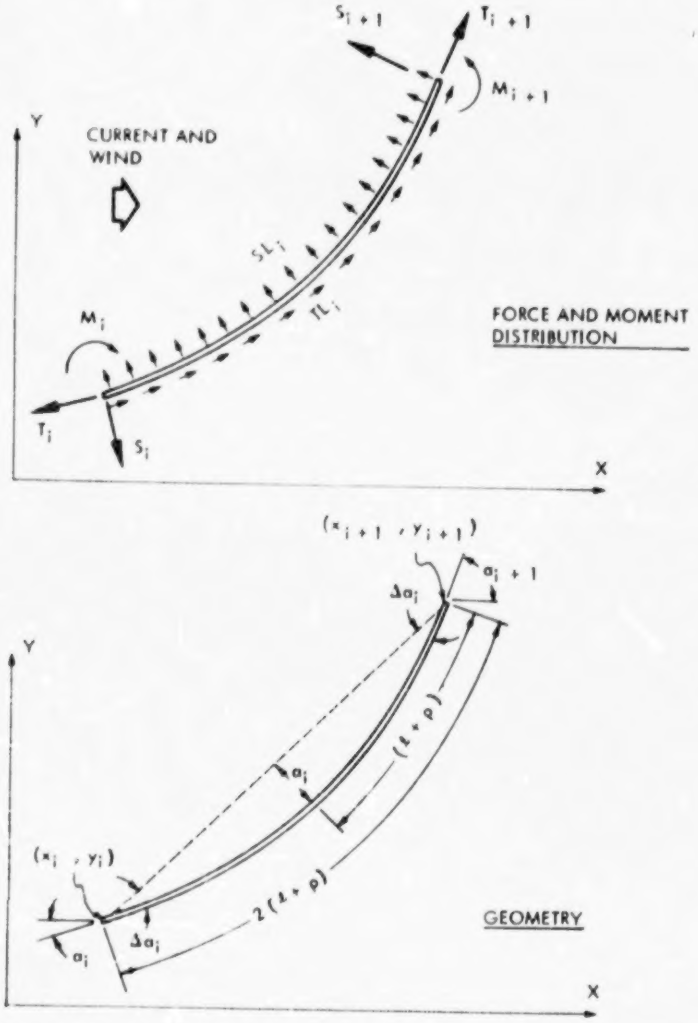


Figure 1. Definition sketch of force and moment distribution, and geometry on a typical boom element.

Recovery. The need for equipment and techniques to recover oil from water surfaces has been recognized for sometime. Unfortunately, existing devices are only suitable for recovering small spills in quiet water areas. They have generally been unadaptable for use on the open ocean. Development of high-capacity recovery equipment specifically designed for open sea use remains to be accomplished.

General Requirements

The nature of massive oil spill cleanup operations at sea dictates that all cleanup equipment meet a number of general requirements.

Transportability. The unpredictability of the location of spill incidents could require large stockpiles of specialized seagoing cleanup equipment near each major trade route, port, or offshore oil production area. From an economic standpoint, the relative infrequency of massive oil spills dictates that the quantity of equipment be minimized. Cleanup equipment should therefore be designed for easy transportation from a centralized storage point to the site of a pollution incident. They should be modularized for air transport to the greatest extent possible.

Ease of Deployment. The quick-spreading nature of oil spills requires cleanup devices be rapidly deployed on the scene. Two steps can be taken to facilitate rapid deployment. First, all equipment should be designed to provide maximum compatability with locally-available boats and ships. In particular, weight handling, towing and equipment assembly requirements should be selected with the capabilities of typical coastal vessels in mind. Second, cleanup equipment should be designed on a total system basis. As an example, a containment system must provide moorings and special deployment and operating equipment as well as a barrier device. Reliance upon locally available sources, or on site fabrication, for special support components should be eliminated.

Systems Integration. Containment and recovery systems should be mutually supporting. Wherever possible, components within either system should be readily adaptable for use with the other. Furthermore, containment systems must be designed to facilitate recovery operations. Conversely, recovery system capacity must be sized to meet the oil-retention capability of the barrier device.

Seagoing Capability. The final general requirement is, of course, that cleanup equipment be able to perform efficiently in high seas. Definition of realistic sea, wind and current conditions under which the various equipment should perform effectively is difficult. However, records of past sea and wind observations can be used to arbitrarily define performance criteria.[2] Analysis of this data has led to the following design goals for open ocean cleanup systems. Systems that can meet these criteria should be capable of performing efficiently 90 per cent of the time off the East Coast of the United States.

1. Perform efficiently in 40 mph winds, 2 knot currents, and 10-foot (significant height) waves.
2. Survive, though not performing effectively, in 60 mph winds, 2-knot currents, and 20 foot (significant height) waves.

Boom Design Considerations

Boom designers are faced with several specific problems if they are to meet the foregoing general requirements.

Cursory examination of spills that have occurred indicates that they fall into two broad categories. The first is related to ship-type accidents. Grounding or collision may result in a sudden catastrophic release of a large amount of oil—at least in the initial phase. The other type of accident may be related to offshore oil production equipment and secondary phases of ship-type accidents.

Type two accidents are categorized by the relatively slow release of large quantities of oil over a prolonged period. The initial grounding of *Torrey Canyon* and the breakup of the *Ocean Eagle* in San Juan Harbor exemplify the first type of accident. The latter stages of the *Torrey Canyon* and the Santa Barbara oil well incident are examples of the second.

Category One accidents demand an extremely rapid response capability. If a containing boom cannot be positioned on site within several hours of an accident, oil will have spread beyond feasible recovery. This means lightweight, readily deployed booms must be provided. Category Two accidents, on the other hand, require heavy weight, heavy duty booms suitable for long-term

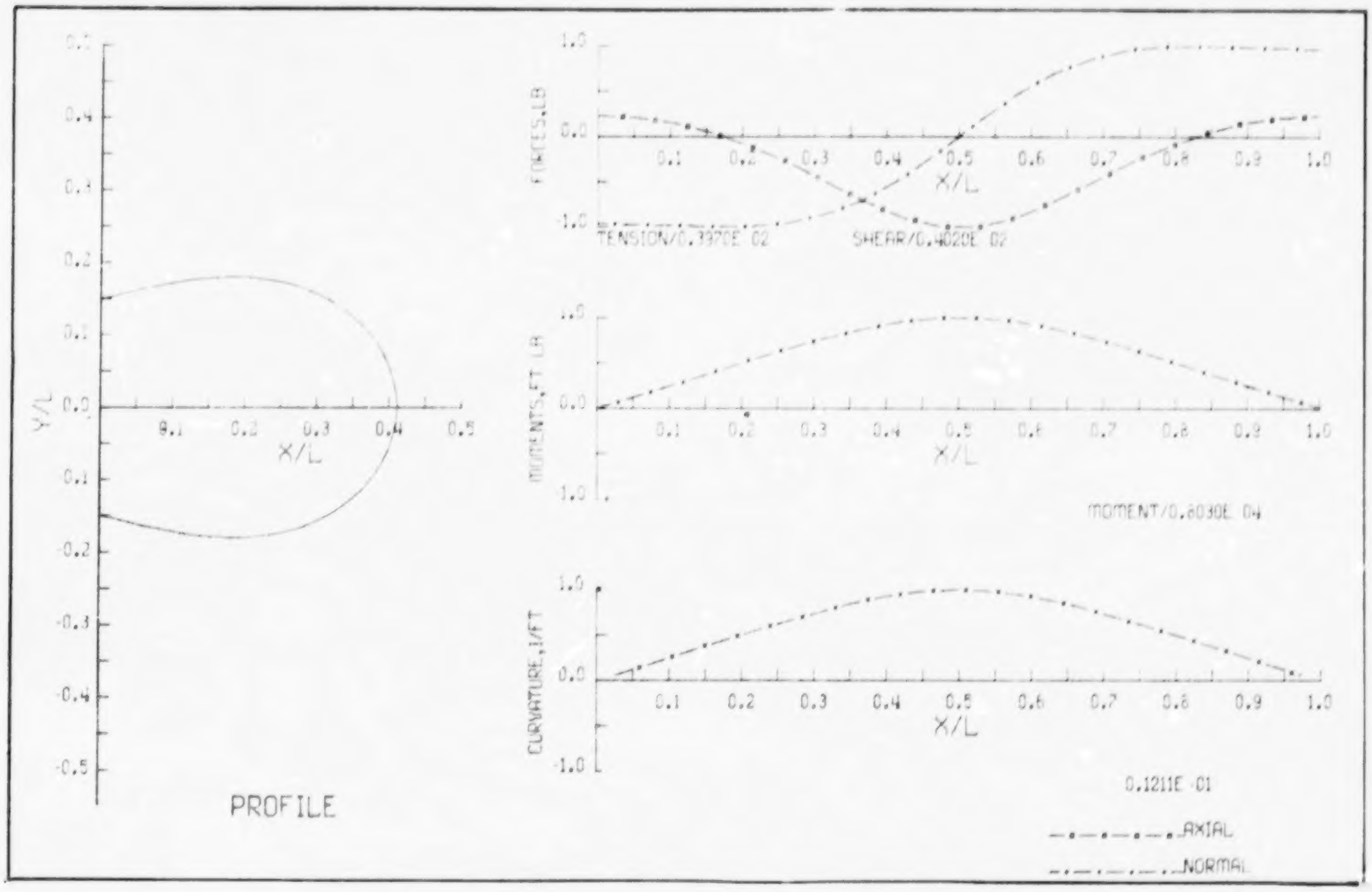


Figure 2. Computed performance with zero current, simulated boom model A.

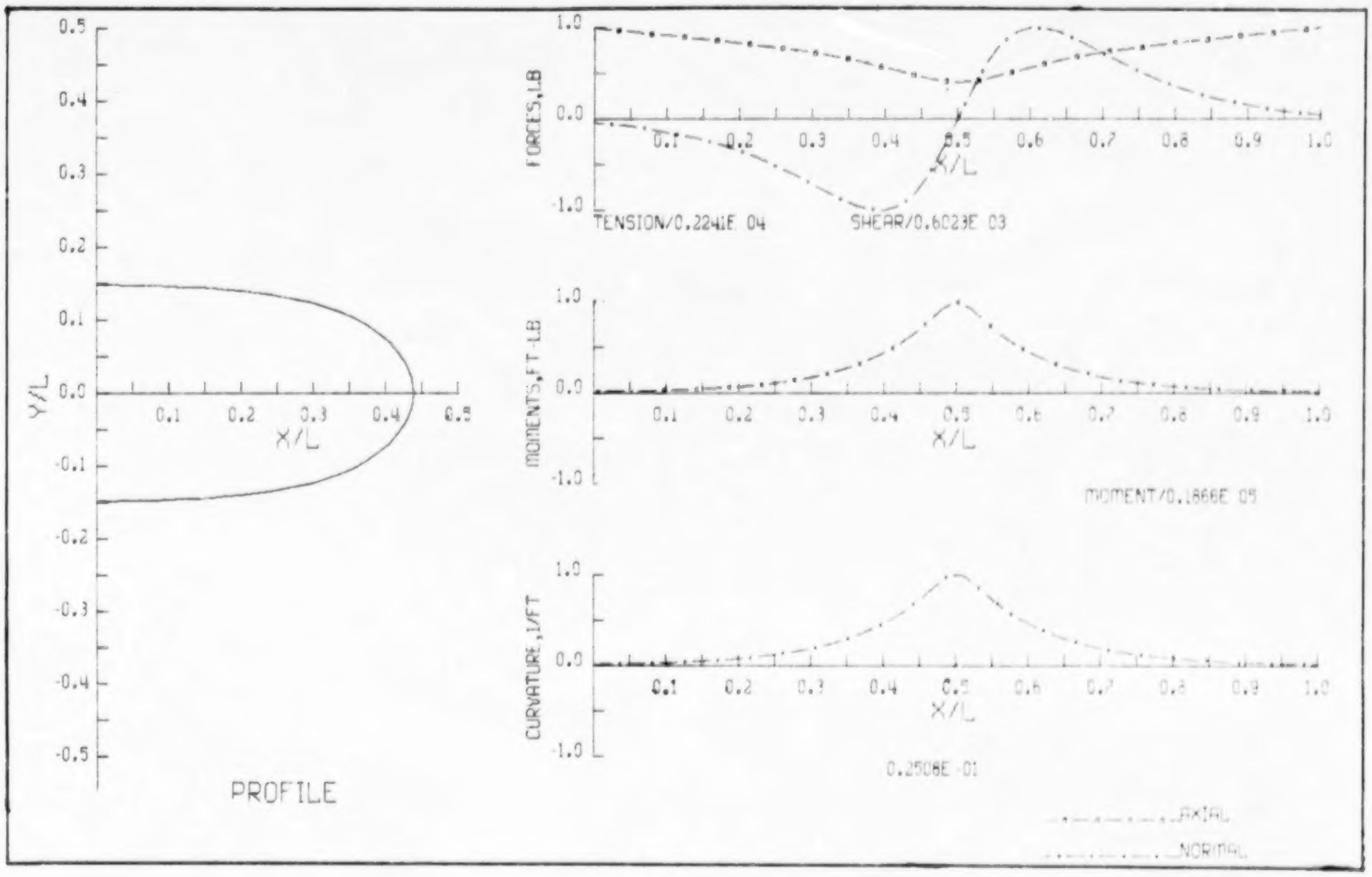


Figure 3. Computed performance with current 1.99 knots (Test 1, fixed mooring, model A, F_D = 0.236).

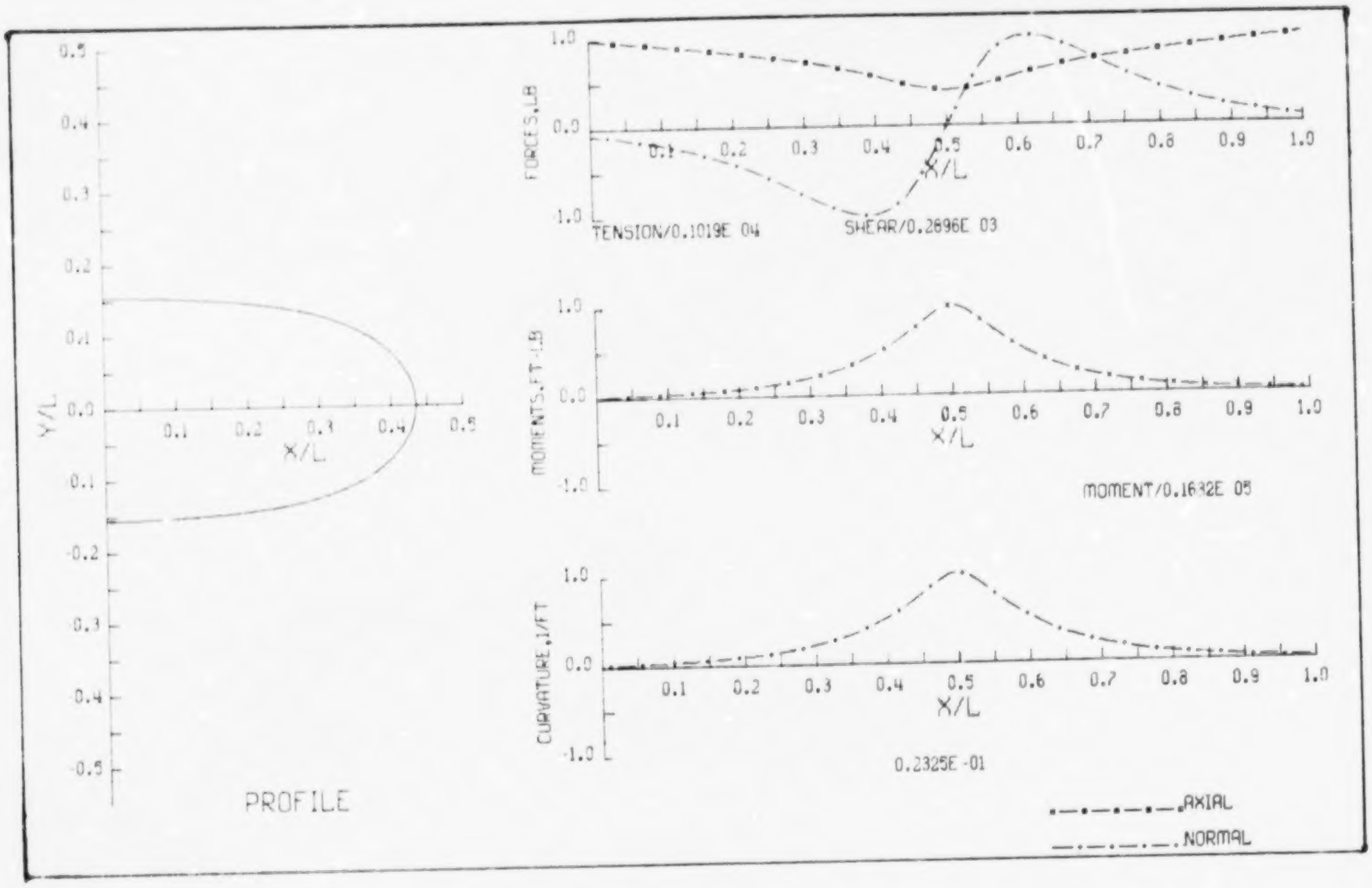


Figure 4. Computed performance with current 1.33 knots (test 2, fixed mooring, model A, $F_D = 0.157$).

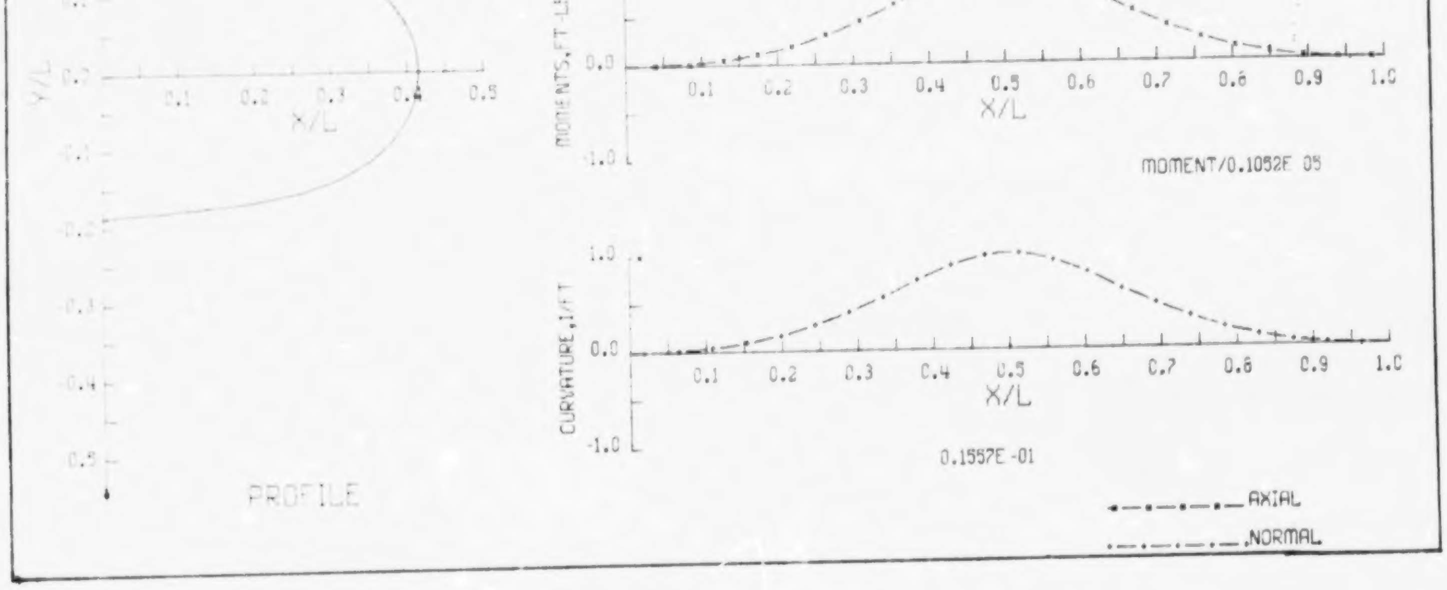


Figure 5. Computed performance with current 0.66 knots (test 3, fixed mooring, model A, $F_D = 0.075$).

emplacement at sea. The performance requirements for each category are significantly different. Therefore, a containment system will probably require several types of boom devices if it is to be successful.

Observations of existing barrier devices indicate two distinct failure modes. They either fail to prevent oil from passing over or under them, or, they break-up under the most moderate sea conditions.[3,4] Unfortunately, little fundamental technical data has been available to solve these problems.

The oil retention capability of a barrier device is influenced by several factors. Wind and current will build a pool of oil against the upstream side of the barrier. However, the built-up pool that can be retained will be significantly less than might be expected based on potential flow or simple hydrostatic analysis. The reasons for this are unclear. The physical phenomena associated with run-under need to be defined. Furthermore, the influence of barrier draft and cross-section geometry in enhancing the thickness of the built-up pool before run-under occurs must be determined. The loss of oil over the top of a boom may be more readily understood. In general they do not respond to passing waves quickly enough and are incapable of conforming to the ocean surface. Thus as a wave train passes, parts of the boom will intermittantly submerge allowing oil to escape. Some optimum combination of freeboard, longitudinal flexibility, and underwater shape must therefore be determined if carryover is to be eliminated.

In any event, a successful barrier device must be based on close examination of the run-under and carryover problems. Optimization of freeboard/draft ratio, cross-section geometry and longitudinal flexibility through theoretical analysis and/or model testing must be accomplished.

Designing high seas booms of adequate strength is another major problem. Except for information developed in connection with moored breakwaters, little data concerning expected stress levels has been available. The U. S. Coast Guard is sponsoring a research study at the firm of Hydronautics, Inc. to provide the needed information. The study will provide basic quantitative engineering data on the performance of oil retention booms in a seaway.

Boom Performance Studies

The aim of the study is to provide designers and evaluators of oil retention booms with information and data to aid in the prediction of boom loads, shapes, and motions. In particular, the research is intended to provide information which will aid in answering the following questions:

1. What are the local loads in an oil retention boom and what are the end or mooring loads in the presence of wind, currents, and seas?
2. What will be the overall configuration assumed by an oil boom under the loads imposed by the sea?
3. What are the motions of the boom in a seaway? In particular, will the boom ever be completely immersed by a wave crest or lift clear of a wave, thus permitting oil to escape?
4. What are the maximum local stresses in an oil retention boom and where along its length will these occur?

The present study is primarily a theoretical analysis of the oil retention boom and will provide information on a large variety of boom configurations and sea conditions. This theoretical analysis is backed up by the results of an experimental program. Towing tank tests conducted on selected boom configurations has provided information which serves to check the accuracy of the theoretical analysis.

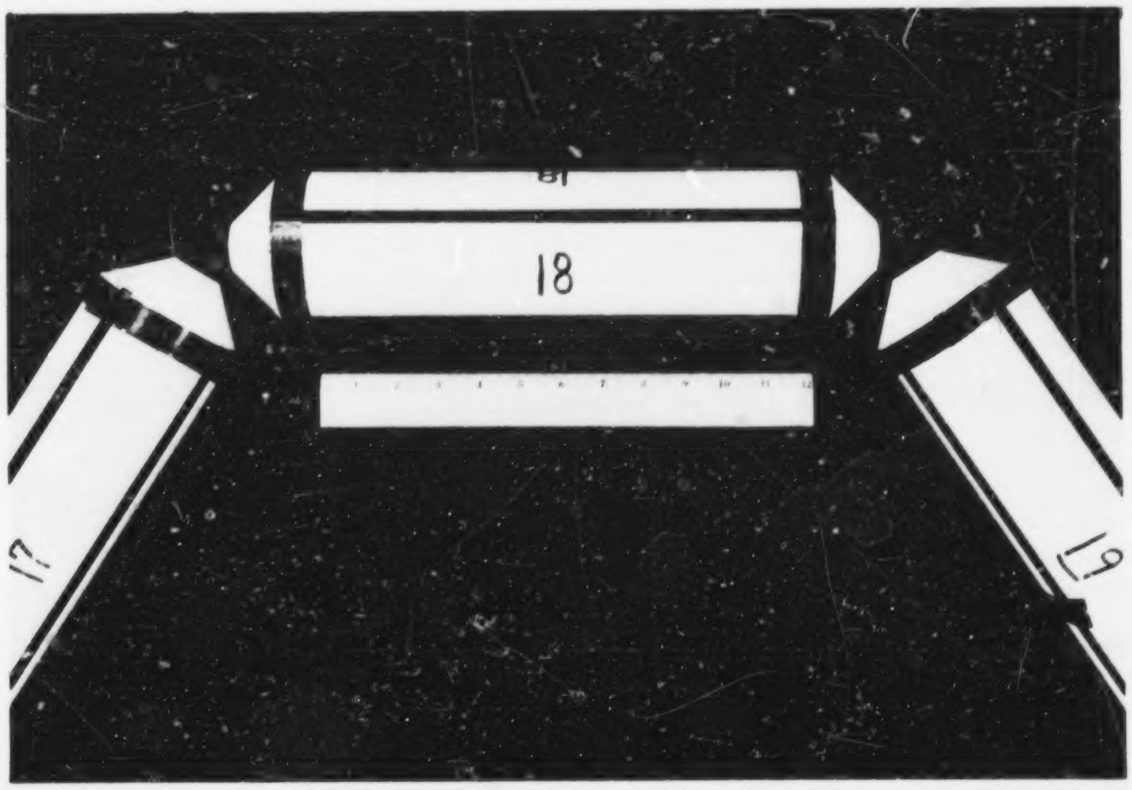


Figure 6. View of model showing details of construction.

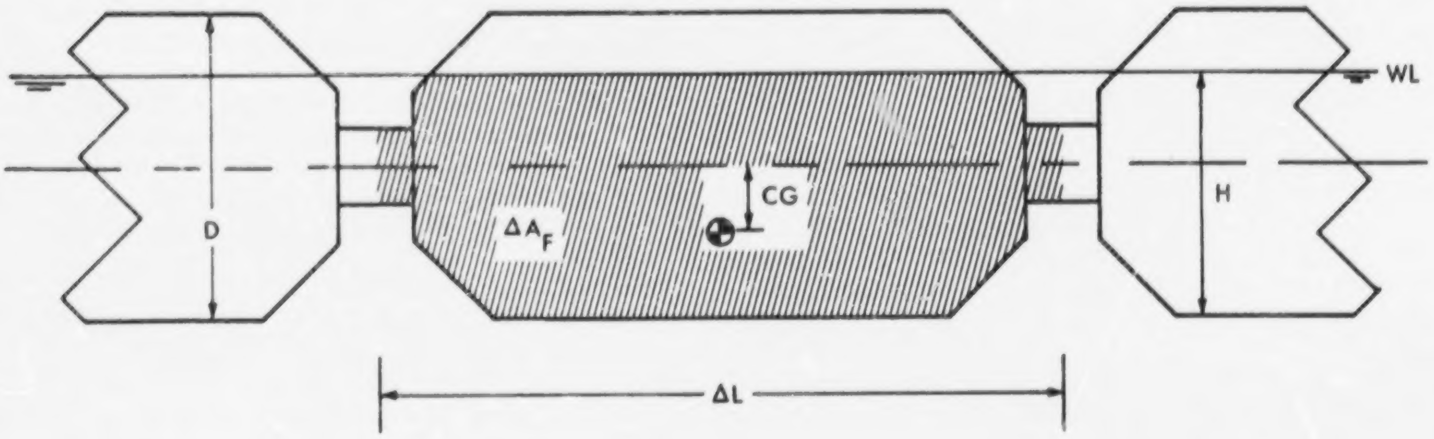


Figure 7. Model definition sketch.

Theoretical Analysis. The complete analytical solution for the motions and loads on an oil retention boom of arbitrary configuration subjected to the loads of wind, current, and an irregular sea is a formidable task. However, the problem can be made tractable and useful results can be obtained if certain simplifying assumptions are made.

The oil retention boom is treated as a continuous elastic beam. It is divided into a large number of imaginary elements, each of which is assumed sufficiently short that angular deflections within its length are small, and that classical linear beam theory will therefore be valid in computing the deflections of each element. It has also been assumed that torsional deflections of the boom are sufficiently small that they produce negligible changes in the horizontal and vertical sectional properties of the boom.

Some important non-linearities are included in the static analysis and should be noted. First, the classical beam deflection and equilibrium equations have been modified to include the influence of tension on deflection. The non-linear coupling of tension and deflection is necessary to permit the solution for booms of small or negligible stiffness. Second, since large deflections are required of the entire boom configuration, all trigometric relations are included in the equations which map the boom geometry.

Third, the changes in hydrodynamic and hydrostatic coefficients which result from a change in immersion of a particular section of the boom are included. That is, changes in hydrodynamic and hydrostatic loads are not considered proportional to displacement but are based on the actual instantaneous position of the boom relative to the sea. This consideration is important in determining the performance of the boom in large seas where the response is highly non-linear and is vital under conditions where the boom might be completely immersed in a wave crest or lift clear of a wave trough—important factors to establish, since either will permit the escape of oil.

The important parameters in determining the performance of an oil retention boom can be divided into four groups: physical properties, hydrodynamic properties, mooring conditions, and environmental conditions. Twenty-seven variables are included in the four groups. Fortunately, the effective number of variables involving boom properties can be reduced by non-dimensionalizing. Specification of variables and non-dimensional analysis are shown in Appendix I.

The numerical solution for the loads and motions of an oil retention boom requires the simultaneous solution of four types of equations. These equations will be illustrated with a two dimensional example. The forces, moments and geometry are defined (Figure 1) for a typical element of the boom. The four types of equations and their basic functions are listed below:

a. "Equilibrium" equations. These equations relate the forces and moments on one end of an element to the force and moments on the other end of the element in terms of the deflections and the applied loads. In the two dimensional case there are three equilibrium equations:

$$(T_i - T_{i+1}) \cos(\Delta\alpha_i) - 2\ell \cdot TL_i + (S_i + S_{i+1})\,\Delta\alpha_i = 0 \tag{1}$$

$$(S_i - S_{i+1}) \cos(\Delta\alpha_i) - 2\ell \cdot SL_i - (T_i + T_{i+1})\,\Delta\alpha_i = 0 \tag{2}$$

$$(M_i - M_{i+1}) - \ell(S_i + S_{i+1}) = 0 \tag{3}$$

b. "Deflection" equations. These equations express the deflections of each element in terms of the applied loads and the forces and moments on the ends

$$\rho_i = \frac{\ell}{EA} \cdot \frac{(T_i + T_{i+1})}{2} \tag{4}$$

$$\gamma_i = \frac{\Delta\alpha_i\,\ell}{2} \tag{5}$$

$$\Delta\alpha_i \left[2 - \frac{\ell^2}{6EI}(T_i + T_{i+1})\right] = \frac{\ell}{EI}(M_i + M_{i+1}) - \frac{\ell^2}{2EI}(S_i - S_{i+1})\cos(\Delta\alpha_i) + \frac{\ell^3}{3EI} \cdot SL_i \tag{6}$$

c. "Shape" equations. These equations relate the position of one end of each element to the position of the other end in terms of its angular position and the deflections within the element. They insure that the end of each element adjacent to another element has the same position and same orientation in space as the end of the mating element (i.e., the boom forms a smooth continuous curve).

$$(x_i - x_{i+1}) + (\ell + \rho)\,[\cos\alpha_i + \cos\alpha_{i+1}] = 0 \qquad (7)$$

$$(y_i - y_{i+1}) + (\ell + \rho)\,[\sin\alpha_i + \sin\alpha_{i+1}] = 0 \qquad (8)$$

$$\alpha_i + 2\Delta\alpha_i - \alpha_{i+1} = 0 \qquad (9)$$

d. "Boundary Conditions" equations. These equations form explicit relations between the forces and moments on the ends of the boom and their location and orientation in space.

$$x_1 \cdot CX_1 - T_1 \cos\alpha_1 + S_1 \sin\alpha_1 = X_1 \cdot CX_1 + \dot{x}_1 \cdot DX_1 + \ddot{x}_1 \cdot MX_1 \qquad (10)$$

$$y_1 \cdot CY_1 - T_1 \sin\alpha_1 - S_1 \cos\alpha_1 = Y_1 \cdot CY_1 + \dot{y}_1 \cdot DY_1 + \ddot{y} \cdot MY_1 \qquad (11)$$

$$\alpha_1 \cdot CA_1 - M_1 = A_1 \cdot CA_1 + \dot{\alpha}_1 \cdot DA_1 + \ddot{\alpha}_1 \cdot MA_1 \qquad (12)$$

$$x_K \cdot CX_K + T_K \cos\alpha_K - S_K \sin\alpha_K = X_K \cdot CX_K + \dot{x}_K \cdot DX_K + \ddot{x}_K \cdot MX_K \qquad (13)$$

$$y_K \cdot CY_K + T_K \sin\alpha_K + S_K \cos\alpha_K = Y_K \cdot CY_K + \dot{y}_K \cdot DY_K + \ddot{y}_K \cdot MY_K \qquad (14)$$

$$\alpha_K \cdot CA_K + M_K = A_K \cdot CA_K + \dot{\alpha}_K \cdot DA_K + \ddot{\alpha}_K \cdot MA_K \qquad (15)$$

where *CX, CY, CA* are the mooring spring constants in x, y and α directions, respectively.

DX, DY, DA are the mooring damping coefficients in x, y, and α respectively.

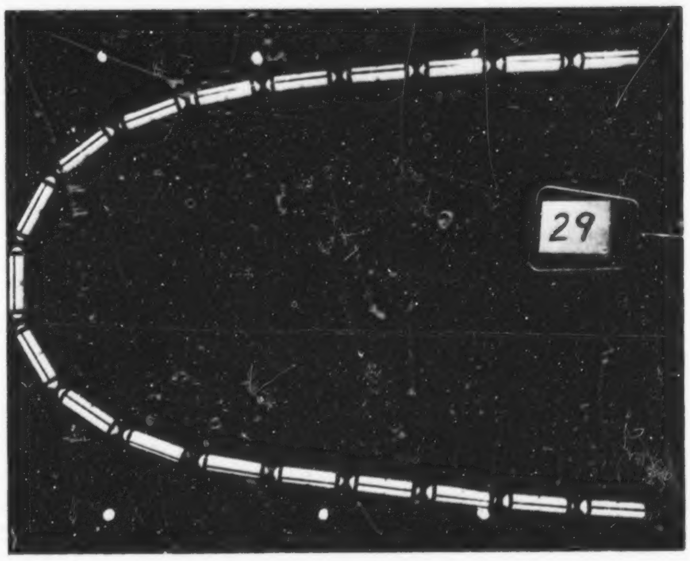
MX, MY, MA are the effective mooring masses in x, y, and α respectively.

X, Y, A are the initial positions of the mooring.

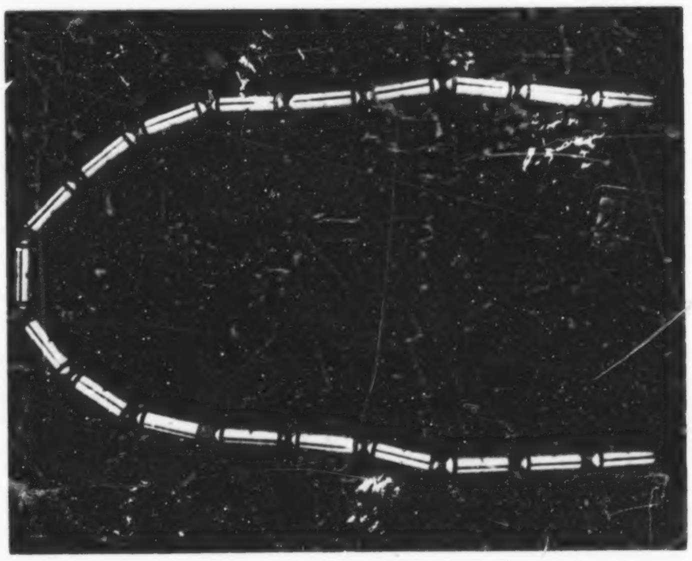
The subscripts 1 and K refer to the conditions on the free ends of 1st element and *K'th* or last element.

The fully expanded two dimensional equations are presented in Appendix I. The three dimensional equations are similar but contain considerably more terms.

The numerical solution of these equations is being carried out on an IBM 1130 digital computer. The equations have been expanded so that the non-linear terms can be expressed with the dominant variables appearing linearly in each equation. They thus form a set of simultaneous linear equations. These equations have been arranged in matrix form and are solved using Guass' reduction method.[5]



a. CALM WATER



b. WAVES

Figure 8. Typical photos of oil boom.

Because of the necessity of expanding non-linear terms, an iterative calculation procedure is required. The calculations for the hydrodynamic loads on the boom, which are a function of the boom position, are based on the boom position in the previous iteration. Initial conditions are provided by assuming the boom floats at its equilibrium waterline and lies in a circular arc curve between its mooring.

The simultaneous equations and computational technique must possess mathematical stability if the iterative solution is to converge. This stability depends on how the non-linear terms are expanded, how the equations are normalized, and the order in which the computations are carried out.

Considerable difficulty has been encountered in obtaining a stable solution for all boom configurations and,

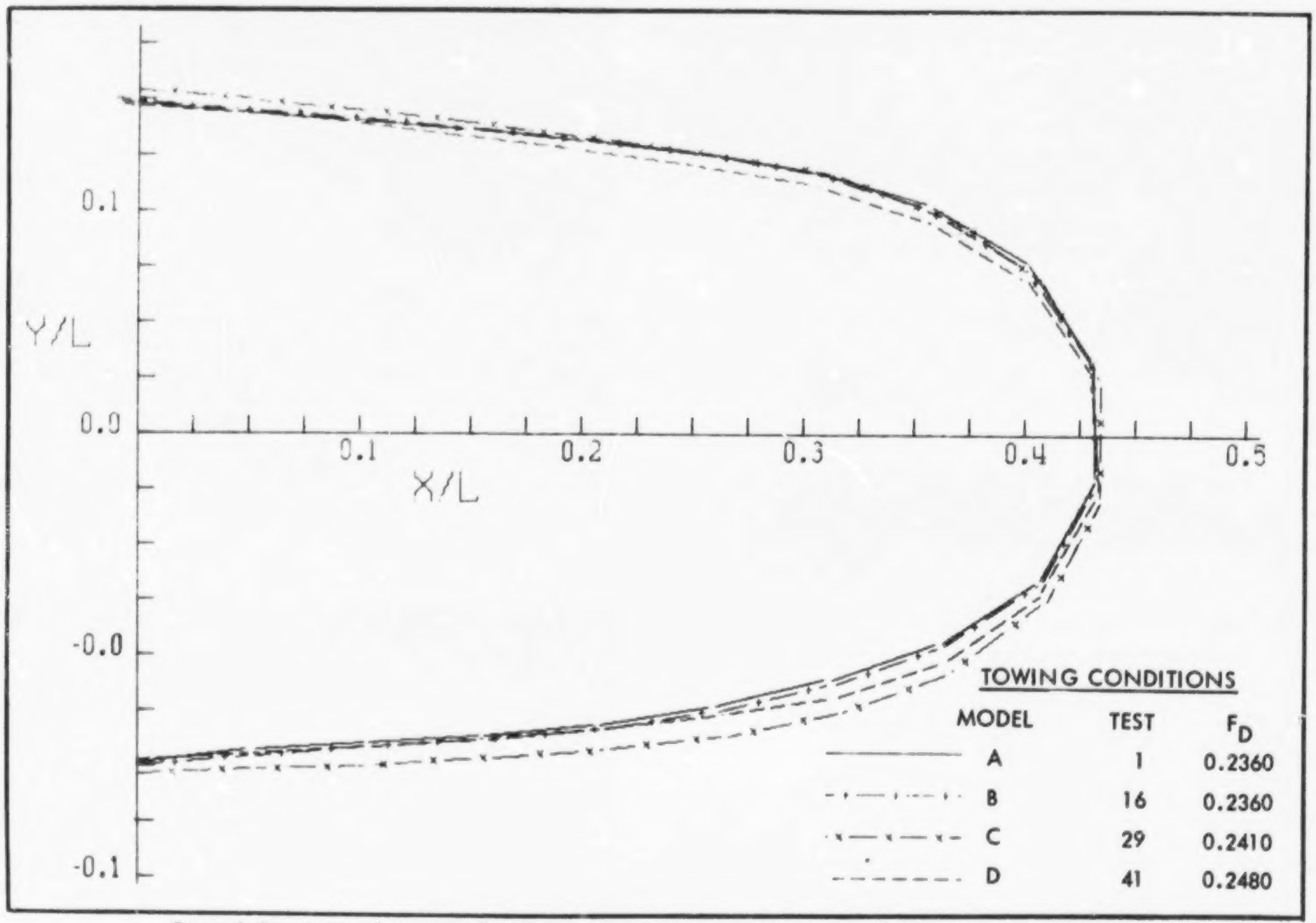


Figure 9. Steady state (calm water) oil boom geometry from model tests, mooring fixed, current 1.99 knots.

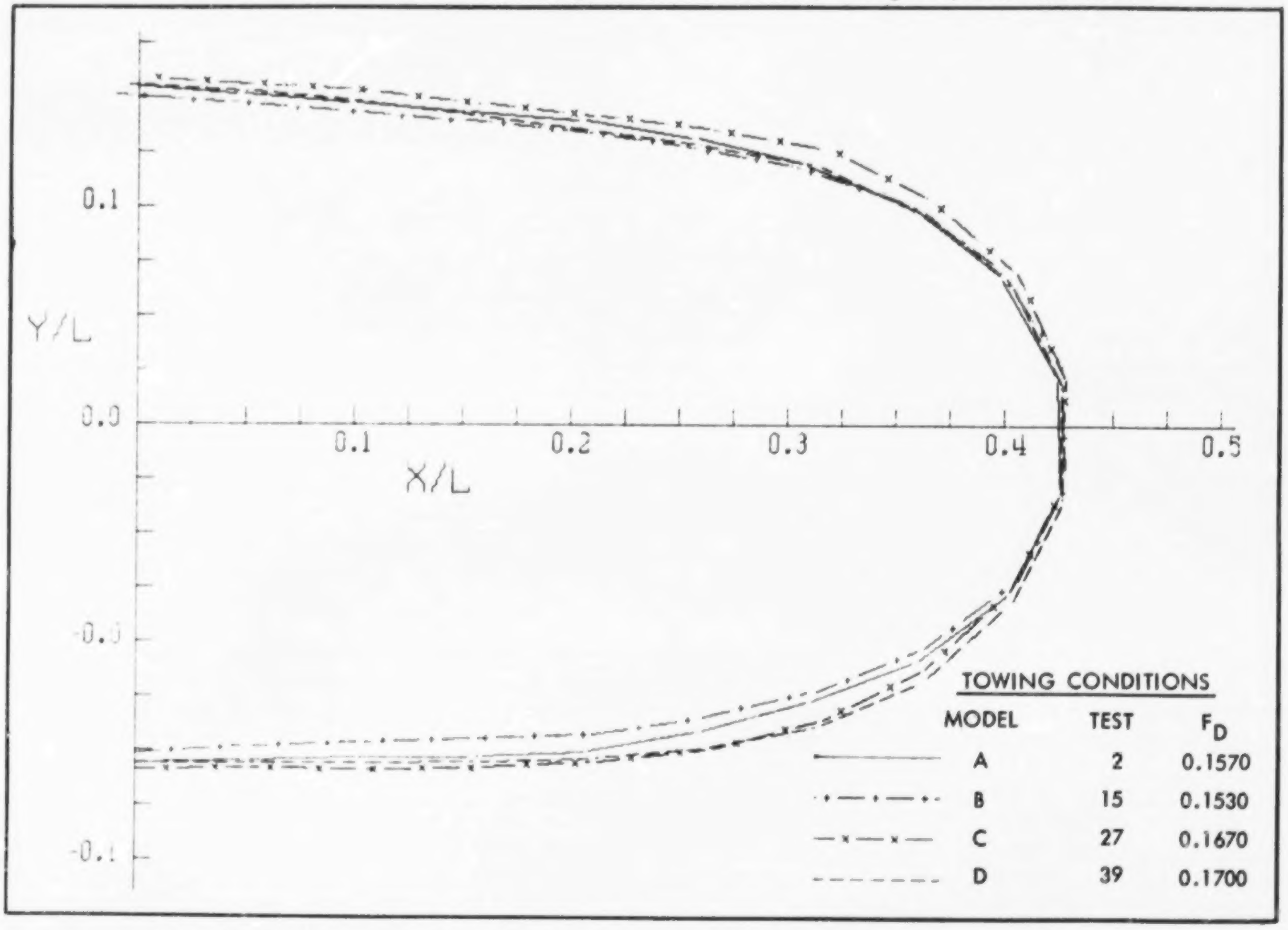


Figure 10. Steady state (calm water) oil boom geometry from model tests, mooring fixed, current 1.33 knots.

unfortunately, the complete six degree of freedoms dynamic program was not operational at the time of this report. This was particularly true for solutions involving booms of low but finite stiffness.

It was found necessary to express the equations in the form of a linear, small amplitude pertubation, about an assumed solution and to include derivatives of all applied load functions with respect to boom position. Calculations can now be carried out for booms of sufficiently low stiffness that for most mooring conditions the influence of shear and bending moment can be considered negligible. For stiffness below this value, the solution for a boom of zero stiffness will provide adequate results.

Although the complete three-dimensional program is not yet operational, two-dimensional, steady-state results have been obtained (Figures 2, 3, 4 and 5). The graph on the left of each of these figures is a plan view of the configuration assumed by the boom. The graph axes are non-dimensionalized in terms of the total boom length. The three graphs on the right present the distribution, along the length of the boom, of the forces, moments and curvature in the boom. These have been normalized in terms of the maximum values for each particular curve: that is, the maximum value is plotted as unity and the other values appear as the fraction of this maximum. The absolute magnitude of the maximum is listed below each curve.

To verify the results of the analytical study, a model test program was carried out. A description of the model program is contained in Appendix II. Figure 6, 7 and 8 depict the model boom.

The boom characteristics and current conditions selected for the calculations whose results are shown in Figures 2, 3, 4 and 5 correspond to some of the model test data. The calculations appear to be in good agreement with the model data.

Comparison of Analytical Results with Model Tests

The two-dimensional, analytical results presented in Figure 3 through 5 correspond to the steady-state tests of model A for currents of 1.99 knots (Test 1), 1.33 knots (Test 2), and 0.66 knots (Test 3). The experimentally-determined boom configurations have been superimposed on the computed configurations (Figure 22, 23, and 24). The agreement between the experimental and computed shape is excellent for the conditions of Test 2 (Figure 23) when allowance is made for the slightly asymmetric shape in the experiment. For Test 1, (Figure 22) the computed shape is slightly fuller than the experimental shape, while in Test 3, (Figure 24) the computed shape is slightly narrower.

The measured and computed drag coefficients for the same three tests are compared in Table 5. The greatest difference occurs in Test 3 where the computed drag is nine per cent less than the measured drag. In general, the agreement between the measured and computed results is good and is within the accuracy of the model test results.

The analytical results for the steady conditions are encouraging and the computation method will provide useful information. However, steady-state results are not sufficient to provide designers and evaluators of oil retention booms with the information they need to predict boom performance in a seaway. The remaining work in the present study is aimed at obtaining quantitative data on the performance of oil retention booms a seaway.

An analysis of the dynamic performance of oil retention booms in a seaway is currently in progress. The analysis assumes that the basic curvature that the boom assumes is the result of the steady wind and current loads. The waves are assumed to cause only small oscillatory pertubations about this basic shape. It is further assumed that the basic radius of curvature of the boom is large compared to wave induced motions and loads will be statistically the same as those on a straight boom with the same tension and orientation to the sea. Linear response operators are being obtained for the boom as a function of boom stiffness, mass, tension and wave frequency. These response operators will be used to calculate the statistical average and maximum expected loads due to waves and the probability of a given length of boom being immersed by a wave crest or lifting clear of a wave trough—important factors to establish, since either will permit the escape of oil.

Current System Development Status and Conclusion

At the beginning of this paper, a three fold approach to cleaning up massive spills was described. Consideration of the general criteria for cleanup systems indicates each approach will require the development of specialized equipment suitable for open sea operation. With this in mind, the U. S. Goast Guard has undertaken a Research and Development program to provide the needed equipment systems.

The initial effort in the program has been concerned with spill amelioration. An air-Delivered Transfer Pumping and Storage System which will facilitate unloading a damaged tanker is now under development. This system will be capable of removing 20,000 tons of crude oil per day from a ship into temporary storage containers. The system is self-sufficient, containing pumps, transfer hose, diesel engines for pump power and storage containers. All components can be air delivered directly to a wreck site. Various subsystem component tests have been completed. Full scale operational testing of a reduced capacity prototype was scheduled for December 1969.

The design of high seas containment systems has also been selected for a major development effort. The research studies to provide engineering design data described above should be completed before the end of the year. At that time, a method to predict boom performance in a seaway will be available. Additionally, the Coast Guard is sponsoring a preliminary design and concept development competition for new containment systems.

At the time of writing, negotiations were underway for the award of multiple design and development contracts. Two types of containment systems are to be developed. One is a lightweight system suitable for rapid deployment. Its intended use is for ship type accidents. The other system is a heavy duty system suitable for long term emplacement at sea. It should solve containment requirements for Santa Barbara-type incidents.

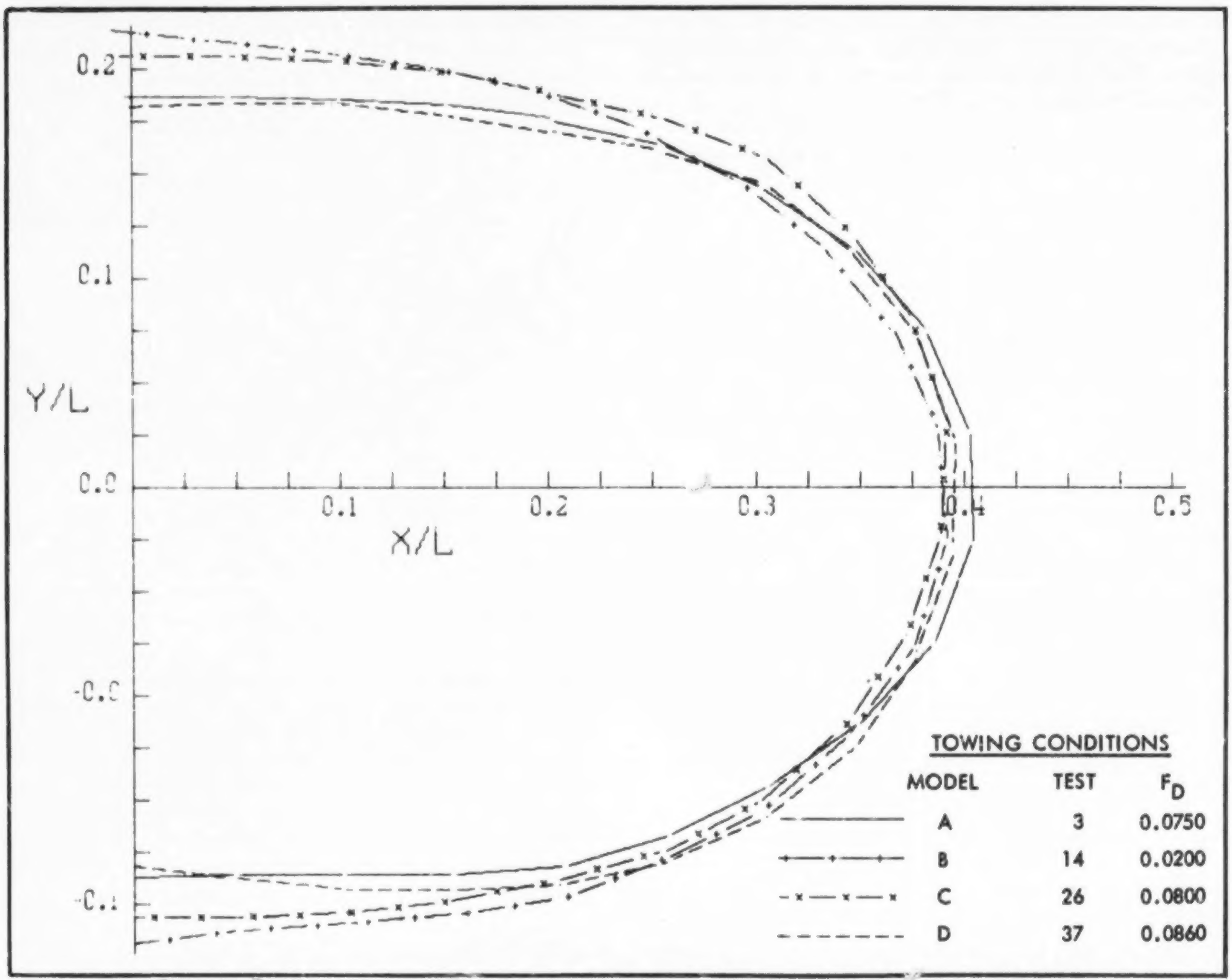


Figure 11. Steady state (calm water) oil boom geometry from model tests, mooring fixed, current 0.66 knots.

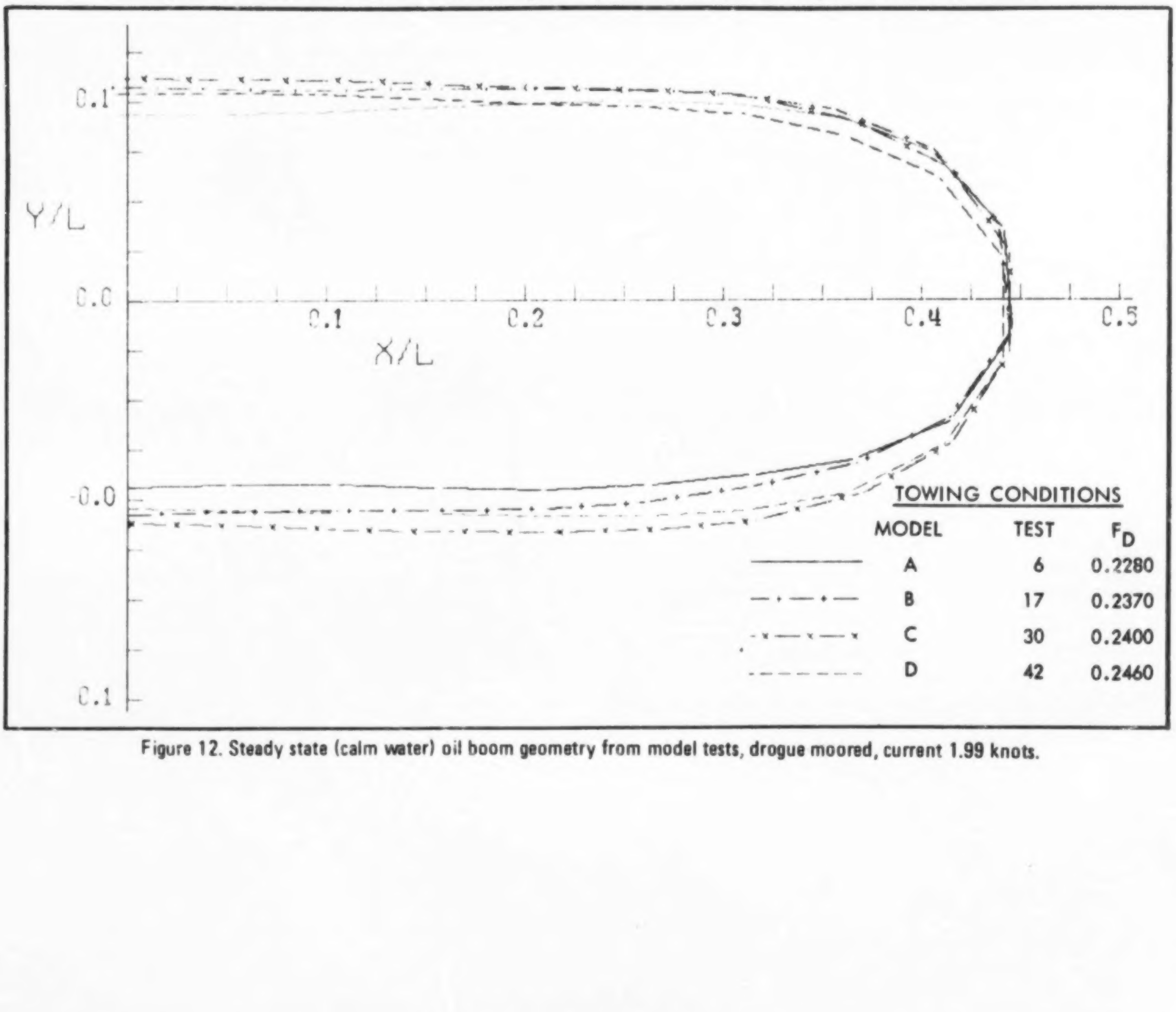


Figure 12. Steady state (calm water) oil boom geometry from model tests, drogue moored, current 1.99 knots.

Both systems must meet the general equipment requirements discussed earlier. Although the boom performance study results will be available, each design effort will be required to develop its own solutions to the other problems inherent in boom design. The results of the design competition are expected late in Spring, 1970.

Work leading to the development of high capacity recovery systems is also proceeding. Background investigations to outline the scope of the problem and set design criteria are underway. In the near future detail design of high seas recovery equipment will be initiated.

Successful completion of the foregoing research and development program should result in a total high seas cleanup capability. At that time, we will have the techniques and equipment needed to properly respond to massive pollution incidents at sea.

APPENDIX I

Parameters Affecting Boom Performance

The important parameters in determining the performance of an oil retention boom can be divided into four groups and are listed below:

Physical Properties

Cross sectional shape
Specific gravity
Center of gravity location
Shear center location
Tensile modulus of elasticity (E)
Shear modulus of elasticity (G)
Vertical section moment of inertia (Iv)
Horizontal section moment of inertia (Ih)
Polar section moment of inertia (J)
Effective structural cross sectional area (A)
Absolute Size
Length

Hydrodynamic Properties

Skin friction coefficient
Drag coefficient for flow normal to boom axis
(same as horizontal damping coefficient)
Vertical damping coefficient
Horizontal added mass coefficient
Vertical added mass coefficient

(Note: These must be defined for both that portion of the boom in the air as well as the portion in the water, and in general, these are all non-linear functions of the local boom positions.)

Mooring Conditions

Mooring configuration (spacing and orientation to the sea)
Mooring spring constants
Mooring damping coefficients
Mooring effective masses

Environmental Conditions

Wind strength
Wind direction
Current strength
Current directions
Seaway spectrum
Dominant wave direction

At present, wind and current are taken to have the same direction and only long crested seas moving in the same direction as the wind and current are being considered. However, this is not an inherent limitation of the analysis and more general sea conditions can be incorporated.

Non-dimensionalization

The effective number of variables involving boom properties can be reduced by non-dimensionalizing. In order to do this, non-dimensional parameters must be found that relate the stiffness of the boom to the buoyant and dynamic forces acting on it in such a way that the correct relation between them is maintained. The deflection of the boom can be non-dimensionalized by expressing the deflection in terms of a characteristic length. Thus:

$$\frac{\delta}{L} \equiv K \frac{FL^2}{EI} \tag{16}$$

where δ is the deflection

L is the characteristic length

K is a function of the load distribution and boundary conditions of the boom

F is the applied load

E is the modulus of elasticity

and I is the section moment of inertia.

Since both buoyant and dynamic forces are involved, these must be non-dimensionalized in such a way that their relative magnitude compared to the elastic stiffness of the boom is maintained. The buoyant and dynamic forces must, of course, be kept in proper proportion relative to each other. For example, a wave passing the boom will change the immersion of the boom and thus change the buoyant force on the boom. The wave also has orbital velocities associated with it and will thus induce dynamic forces proportional to the Froude number squared.

$$(\text{Froude number})^2 = \frac{V^2}{gL} \tag{17}$$

where V is a characteristic velocity (wind or current)

and g is the acceleration of gravity

Thus to maintain the relation of the dynamic and buoyant forces, the Froude number must be constant. Since the acceleration of gravity (g) is fixed:

$$V^2 \sim L \tag{18}$$

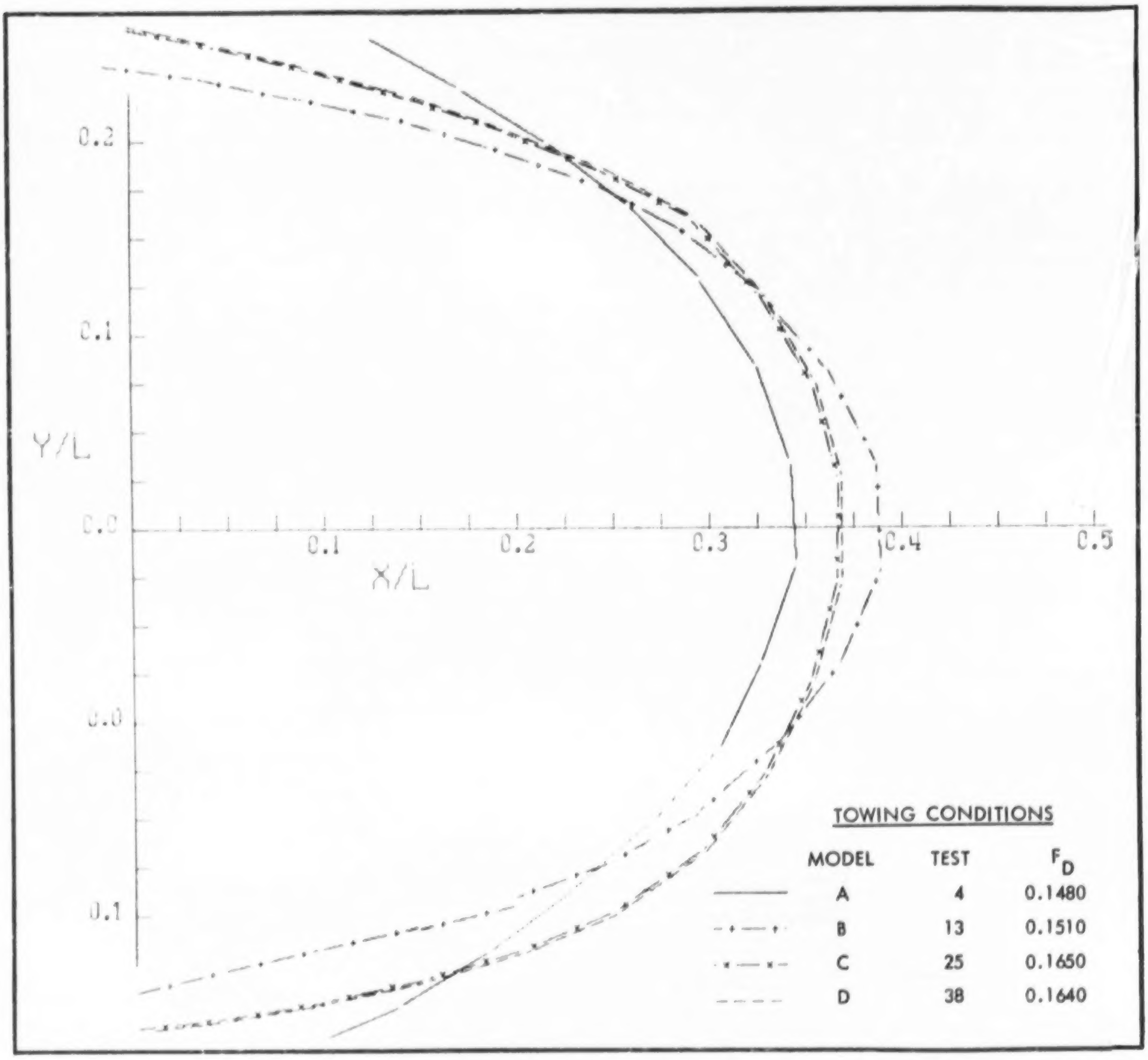


Figure 13. Steady state (calm water) oil boom geometry from model tests, drogue moored, current 1.33 knots.

The Reynolds number, a measure of the relative magnitude of the dynamic forces compared to the viscous forces, must also be considered. Reynolds number is expressed as:

$$(\text{Renolds number}) = \frac{\rho V L}{\mu} \qquad (19)$$

where ρ is the fluid density (air or water)
μ is the fluid viscosity (air or water)

For a given sea condition ρ and μ are fixed, thus, for a constant Reynolds number:

$$V \sim \frac{1}{L} \qquad (20)$$

This result is, of course, incompatible with equation (18). Fortunately, the major influence of viscosity is only to modify the dynamic coefficients. The magnitude of this effect is usually small compared to the influence of the buoyant forces. In fact, within the range of practical boom sizes (say 2 to 10 feet in height) the influence of a change in Reynolds number will be negligible.

Non-dimensionalizing can therefore be accomplished using the Froude number to provide the required relation between dynamic and buoyant forces, i.e., between V and L.

Since the buoyant forces (F_b) are proportional to L^3 and dynamic forces of wind (F_w) and current (F_c) are proportional to V^2L^2, boom deflections per unit length due to buoyancy (δ_b), wind (δ_w), and current (δ_c) can be expressed with the aid of Equation (16) as:

$$\frac{\delta_b}{L} = K_B \frac{F_b L^2}{EI} \sim \frac{L^5}{EI} \qquad (21)$$

$$\frac{\delta_w}{L} = K_w \frac{F_w L^2}{EI} \sim \frac{L^5}{EI}$$

$$\frac{\delta_c}{L} = K_c \frac{F_c L^2}{EI} \sim \frac{L^5}{EI}$$

Thus, geometrically similar booms of different absolute size will behave the same if the ratio L^5/EI is maintained and wind and current velocities are adjusted proportional to $\sqrt{L}$.

Absolute size can now be eliminated as a parameter if we define a non-dimensional stiffness (S'), a non-dimensional wind speed (V'_w), a non-dimensional current (V'_c) and a non-dimensional wave height (h'):

$$S' = \frac{EI}{\rho_w g L^5} \tag{22}$$

$$V'_w = \sqrt{\frac{1/2\ \rho_a\ V_w^2 L^4}{EI}}$$

$$V'_c = \sqrt{\frac{1/2\ \rho_w\ V_c^2\ L^4}{EI}}$$

where ρ_w is the density of water
ρ_a is the density of air
h is the wave height

To apply this scaling to the real sea one further assumption is made. That is, that the scaled energy distribution of the waves in one sea state is the same as in another sea state. (e.g., sea state 3 is a scale model of, say, sea state 4).

While this non-dimensionalizing is, of course, not necessary it does provide a useful framework for comparing the performance of booms of slightly differing sizes.

Fully Expanded Two Dimensional Equations

The fully expanded two dimensional equations are presented below. The three dimensional equations are similar but contain considerably more terms. Terms marked $(^{-})$ are evaluted from the previous iteration and form the base for the linear expansion

Equilibrium Equations

$$(T_i - T_{i+1}) \cos(\Delta\bar{\alpha}_i) + (S_i + S_{i+1})\,\Delta\bar{\alpha}_i$$

$$+ \Delta\alpha_i (\bar{S}_i + \bar{S}_{i+1}) - \ell(\alpha_i + \alpha_{i+1}) \frac{dTL}{d\alpha} =$$

$$\Delta\bar{\alpha}_i (\bar{S}_i + S_{i+1}) + 2\ell \cdot TL - \ell(\bar{\alpha}_i + \bar{\alpha}_{i+1}) \frac{dTL}{d\alpha} \tag{23}$$

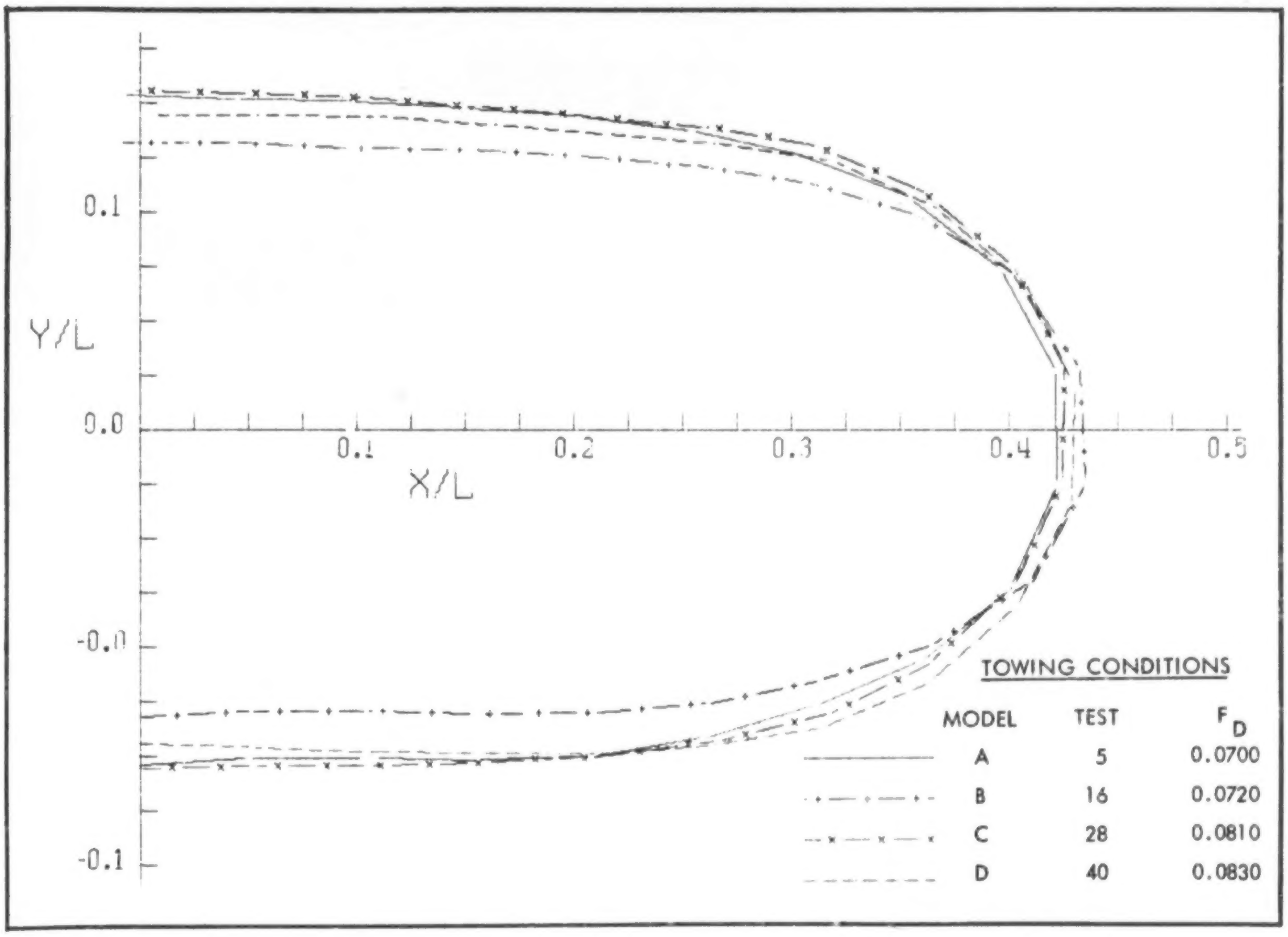


Figure 14. Steady state (calm water) oil boom geometry from model tests, drogue moored, current 0.66 knots.

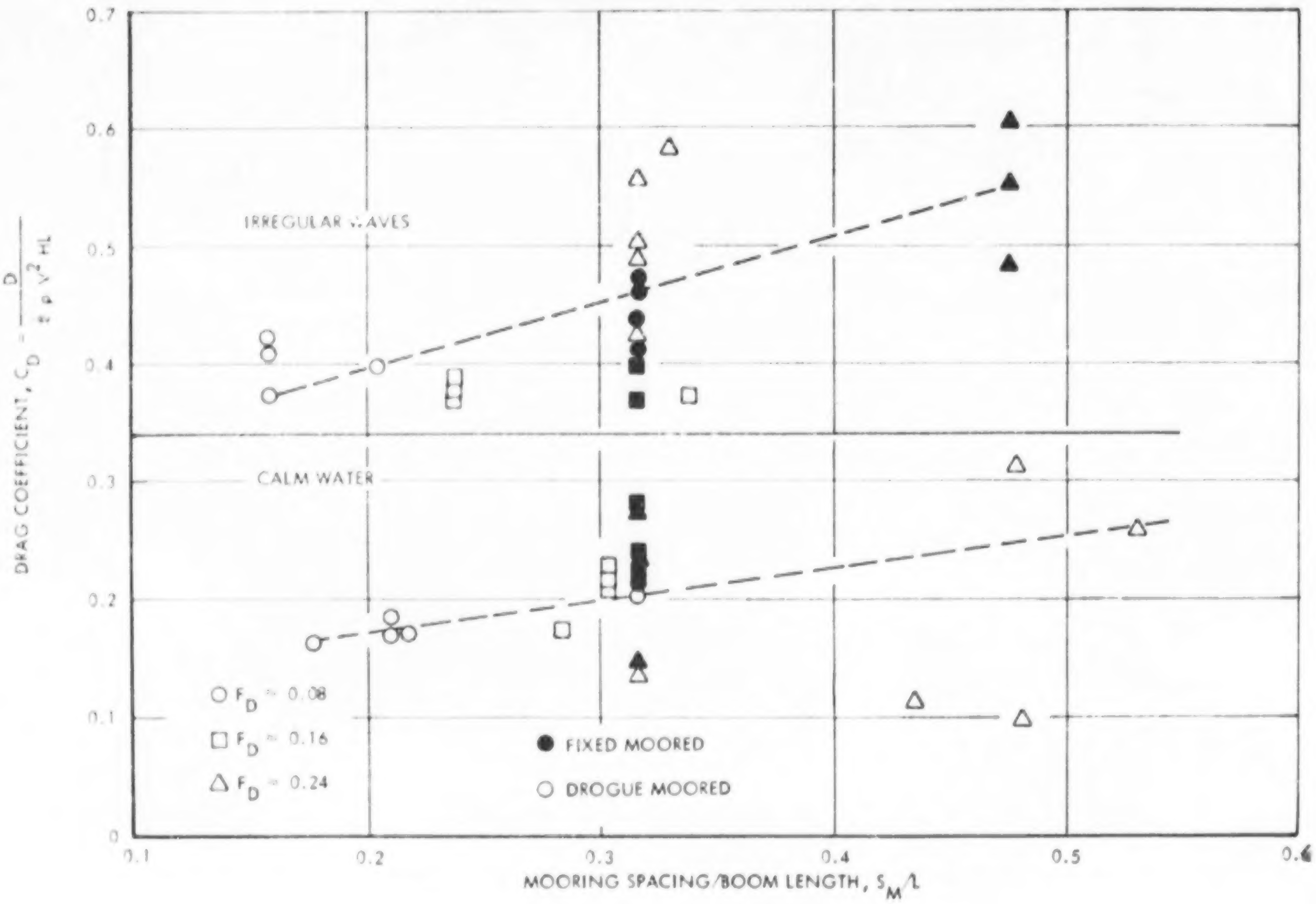


Figure 15. Oil boom model test drag data.

$$(S_i - S_{i+1}) \cos(\Delta\bar{\alpha}_i) - (T_i + T_{i+1})\, \Delta\bar{\alpha}_i + \Delta\alpha_i (\overline{T}_i + \overline{T}_{i+1})$$

$$- \ell (\alpha_i + \alpha_{i+1}) \frac{dSL}{d\alpha} = - \Delta\bar{\alpha}_i (\overline{T}_i + \overline{T}_{i+1})$$

$$+ 2\ell \cdot SL - \ell (\bar{\alpha}_i + \bar{\alpha}_{i+1}) \frac{dSL}{d\alpha} \qquad (24)$$

$$M_i - M_{i+1} - \ell (S_i + S_{i+1}) = 0 \qquad (25)$$

Deflection Equations

$$\rho_i = \frac{\ell}{EA} \cdot \frac{(T_i + T_{i+1})}{2} \qquad (26)$$

$$\gamma_i = \frac{\Delta\alpha_i\, \ell}{2} \qquad (27)$$

$$\Delta\alpha_i = \left[2 - \frac{\ell^2}{6EI} (\overline{T}_i + \overline{T}_{i+1}) \right] -$$

$$\frac{\ell^2}{6EI} (T_i + T_{i+1})\, \Delta\bar{\alpha}_i - \ell (\alpha_i + \alpha_{i+1}) \frac{dSL}{d\alpha} =$$

$$\frac{\ell}{EI} (M_i + M_{i+1}) \cos(\Delta\alpha_i) - \frac{\ell^2}{2EI} (S_i + S_{i+1}) \cos(\Delta\alpha_i) + \frac{\ell^3}{3EI} \cdot SL - \ell (\overline{\alpha}_i + \alpha_{i+1}) \frac{dSL}{d\alpha} \qquad (28)$$

Shape Equations

$$(x_i - x_{i+1}) - \ell (\alpha_i \sin \bar{\alpha}_i + \alpha_{i+1} \sin \bar{\alpha}_{i+1})$$

$$+ (\ell + \rho) (\cos \bar{\alpha}_i + \cos \bar{\alpha}_{i+1}) =$$

$$- \ell (\overline{\alpha}_i \sin \bar{\alpha}_i + \bar{\alpha}_{i+1} \sin \bar{\alpha}_{i+1}) \qquad (29)$$

$$(y_i - y_{i+1}) + \ell (\alpha_i \cos \bar{\alpha}_i + \alpha_{i+1} \cos \bar{\alpha}_{i+1})$$

$$+ (\ell + \rho) (\sin \bar{\alpha}_i + \sin \bar{\alpha}_{i+1}) =$$

$$\ell (\bar{\alpha}_i \cos \bar{\alpha}_i + \bar{\alpha}_{i+1} \cos \overline{\alpha}_{i+1}) \qquad (30)$$

$$\alpha_i + 2\Delta\alpha_i - \alpha_{i+1} = 0 \qquad (31)$$

Boundary Condition Equations

$$x_1 \cdot CX_1 - T_1 \cos \bar{\alpha}_1 + S_1 \sin \bar{\alpha}_1$$

$$+ (\alpha_1 - \bar{\alpha}_1) (\overline{T}_1 \sin \bar{\alpha}_1 + \overline{SN} \cos \bar{\alpha}_1) =$$

$$x_1 \cdot CX_1 + \dot{x} \cdot DX_1 + \ddot{x} \cdot MX_1 \qquad (32)$$

$$y_1 \cdot CY_1 - T_1 \sin \bar{\alpha}_1 - S_1 \cos \bar{\alpha}_1$$
$$+ (\alpha_1 - \bar{\alpha}_1)(-\bar{T}_1 \cos \bar{\alpha}_1 + \overline{SN} \sin \bar{\alpha}_1) =$$
$$Y_1 \cdot CY_1 + \dot{y} \cdot DY_1 + \ddot{y} \cdot MY_1 \quad (33)$$

$$\alpha_1 \cdot CA_1 - M_1 =$$
$$A_1 \cdot CA_1 + \dot{\alpha}_1 \cdot DA_1 + \ddot{\alpha}_1 \cdot MA_1 \quad (34)$$

$$x_K \cdot CX_K + T_K \cos \bar{\alpha}_K - S_K \sin \bar{\alpha}_K$$
$$- (\alpha_K - \bar{\alpha}_K)(\bar{T}_K \sin \bar{\alpha}_1 + \overline{SN} \cos \bar{\alpha}_K) =$$
$$X_K \cdot CX_K + \dot{x} \cdot DX_K + \ddot{x} \cdot MX_K \quad (35)$$

$$y_K \cdot CY_K + T_K \sin \bar{\alpha}_1 + S_K \cos \bar{\alpha}_K$$
$$+ (\alpha_K - \bar{\alpha}_K)(\bar{T}_K \cos \bar{\alpha}_K - \overline{SN} \sin \bar{\alpha}_K) =$$
$$Y_K \cdot CY_K + \dot{y} \cdot DY_K + \ddot{v} \cdot MY_K \quad (36)$$

$$\alpha_K \cdot CA_K + M_K = A_K \cdot CA_K + \dot{\alpha}_K DA_K + \ddot{\alpha}_K \cdot MA_K \quad (37)$$

APPENDIX II

Oil Boom Model Tests

To verify the results of the analytical study, a model test program was conducted. The tests were conducted and the following discussion was prepared by W. L. Lindenmuth. A description of the model, test procedures, and results follows:

The Model. A scale model of an oil boom must be dynamically as well as geometrically similar to the prototype. To satisfy dynamic (Froude) scaling, the "bending stiffness," EI, and "torsional rigidity," GJ, of the model must be scaled to the fifth power of the scale ratio λ:

$$\lambda = \frac{Dp}{Dm} = \frac{Lp}{Lm} \quad (38)$$

where

D = diameter, ft

L = length, ft

p = subscript denoting "prototype"

m = subscript denoting "model"

A non-dimensional stiffness S' may be defined as one that must be constant for both model and prototype:

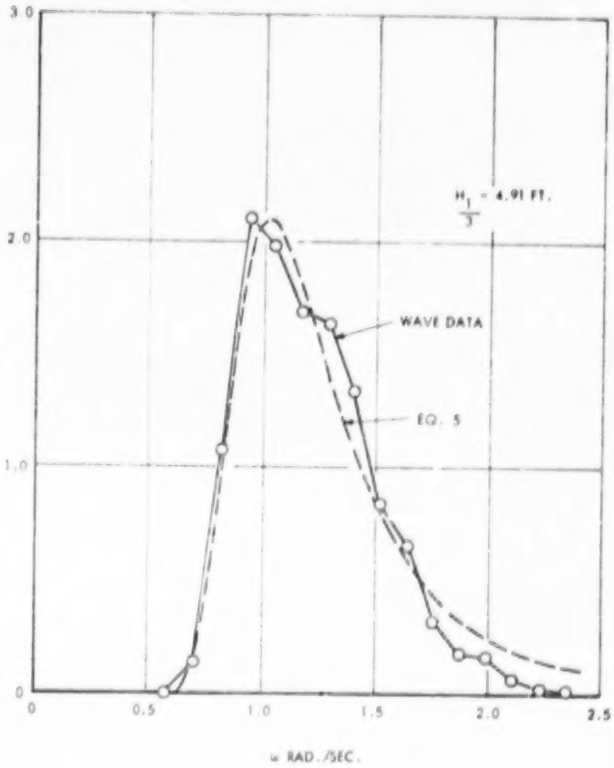


Figure 16. Sea state 3, model test wave spectrum.

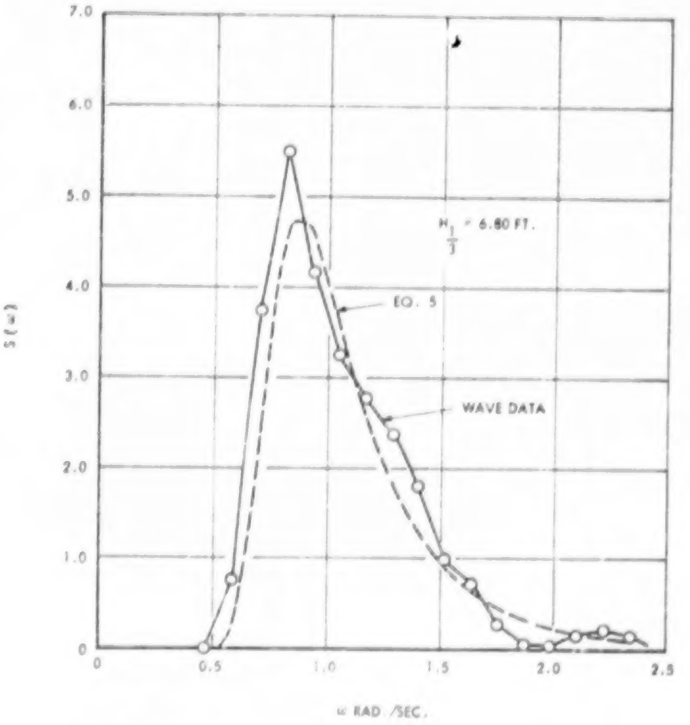


Figure 17. Sea state 4, model test wave spectrum.

$$S' = \left(\frac{EI}{\rho g D^5}\right)_m = \left(\frac{EI}{\rho g D^5}\right)_p \quad (39)$$

where

ρ = mass density of water, slug-ft

g = acceleration of gravity, ft-sec

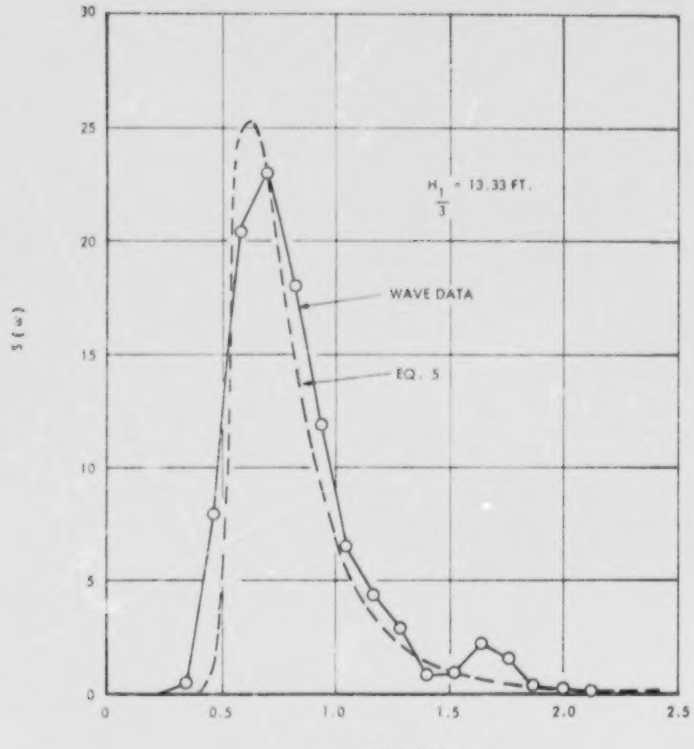


Figure 18. Sea state 5, model test wave spectrum.

Thus,

$$(EI)_m = \frac{(EI)_p}{\lambda^5} \cdot \left(\frac{\rho_m}{\rho_p}\right) \tag{40}$$

GJ may be substituted for EI in Equations (39) and (40).

The ratio ρ_m/ρ_p in Equation (40) is a correction for the difference in density of fresh water (model) and salt water (prototype) ≈ 0.97.

The bending stiffness and torsional rigidity of a realistic oil retention boom model are quite small due to the dynamic scaling criterion. The model boom must be extremely flexible to simulate a full size boom. To achieve this flexibility with materials that were readily available, the model boom was fabricated of wooden 15-inch long cylindrical segments connected by 1-inch joints of polyvinyl chloride (PVC) tubing. All flexing of the model occurs in the 5/8-inch diameter joints. The model consists of 19 segments and 18 joints, giving a total model length L = 25.25 ft.

The segment diameter = 3.60 inches. However, the ends of the segments are tapered with 45° cones to permit the joints to bend to 90°.

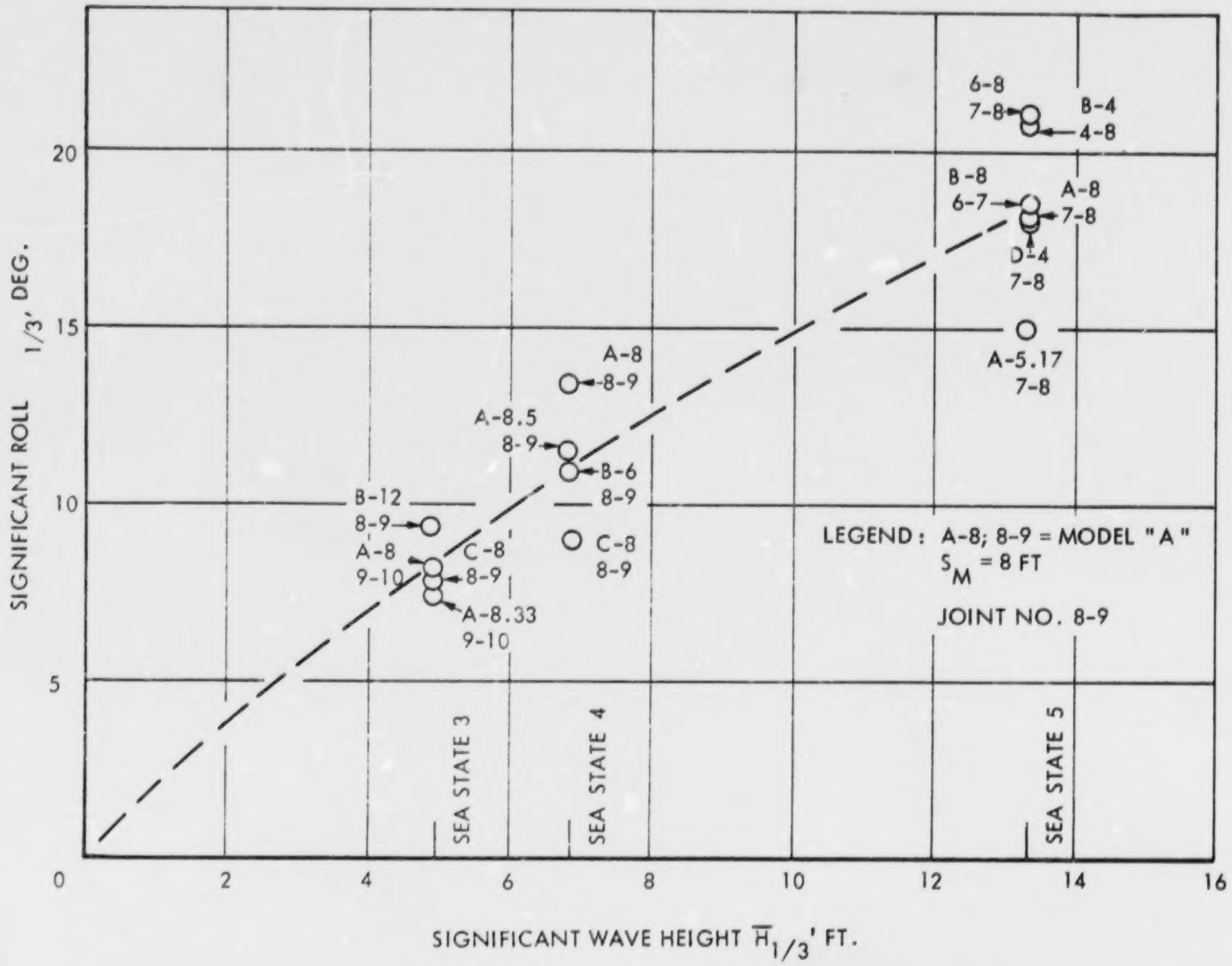


Figure 19. Significant roll motion in irregular waves.

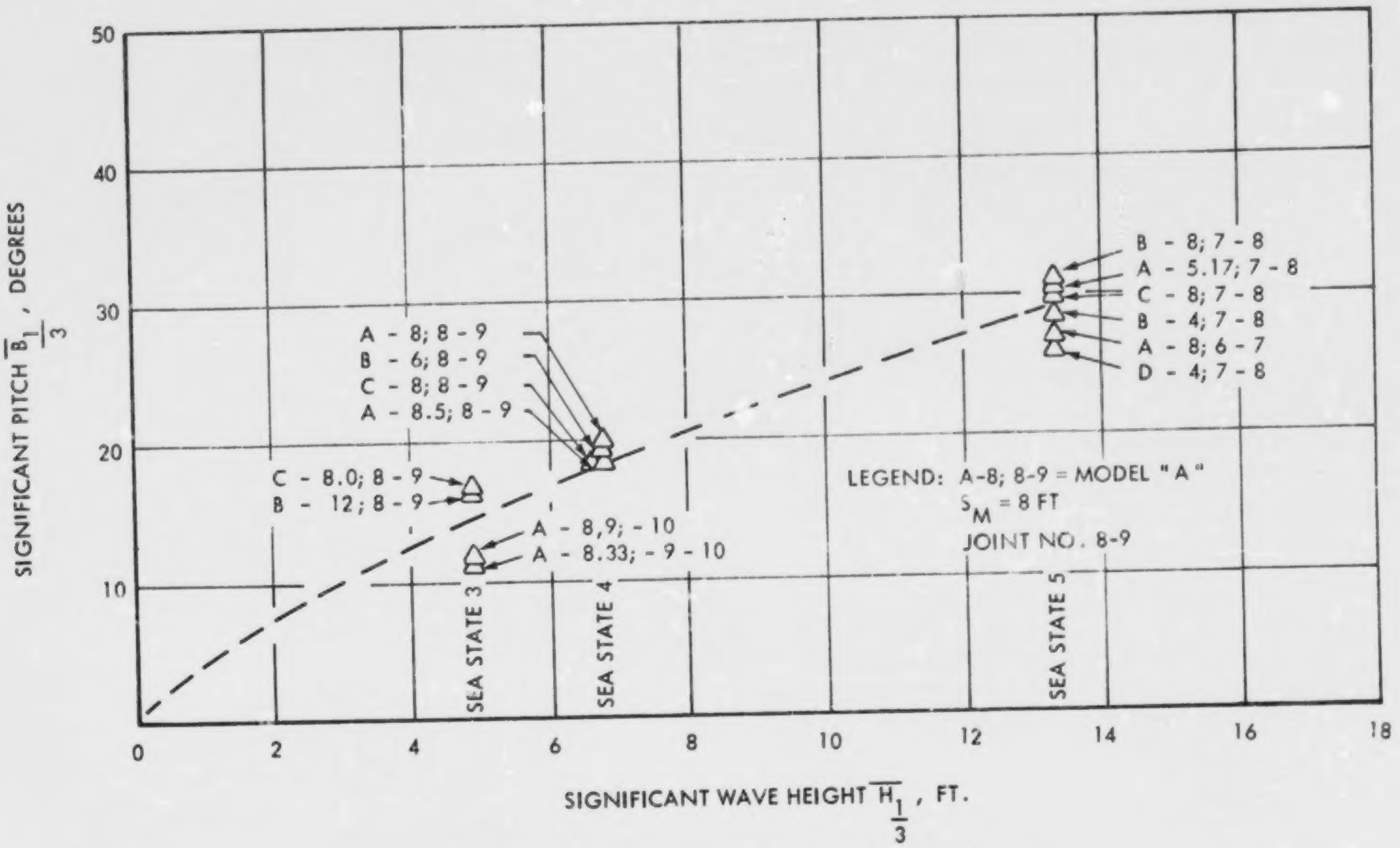


Figure 20. Significant pitch motion in irregular waves.

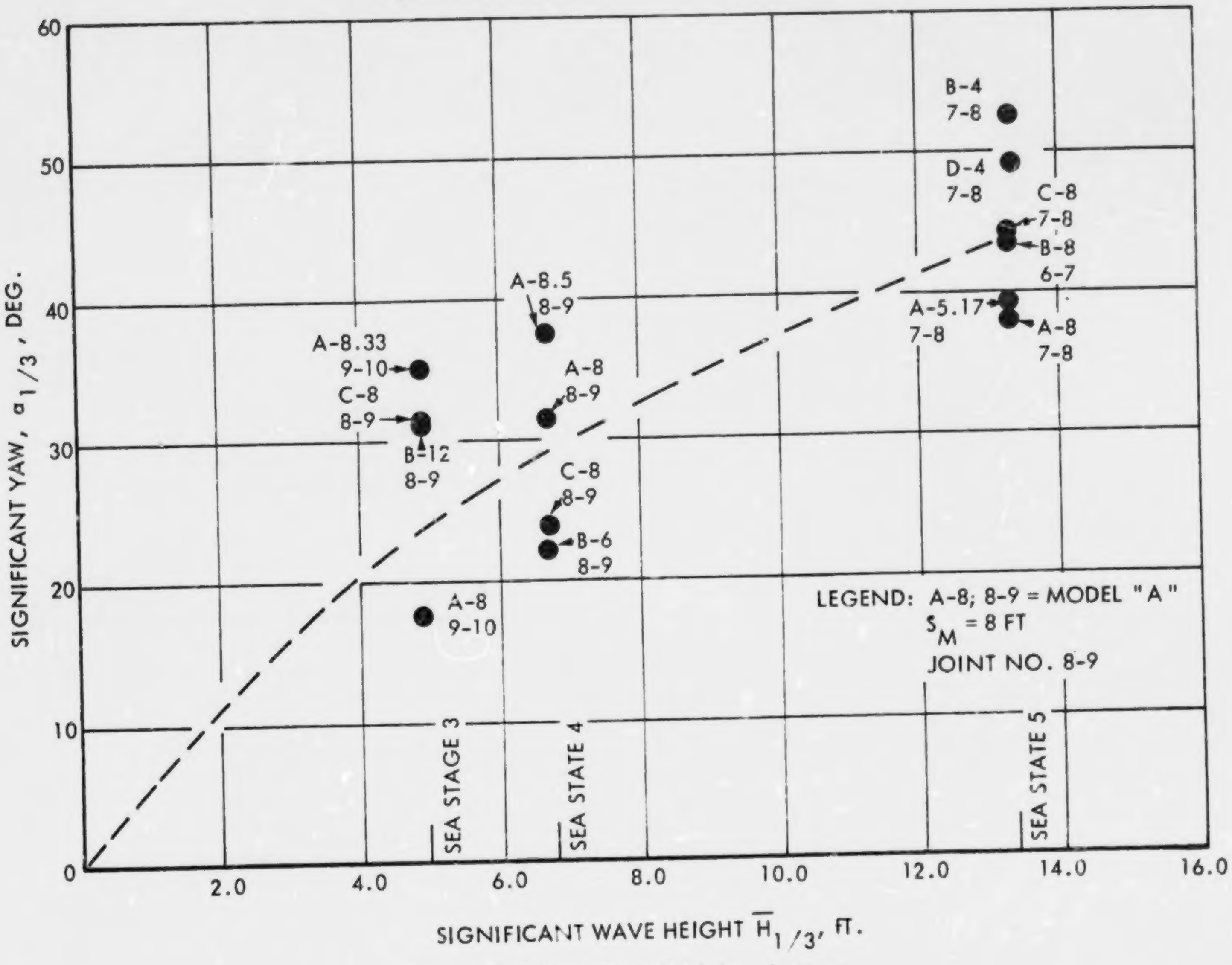


Figure 21. Significant yaw motion in irregular waves.

Each segment has four slots evenly spaced around its perimeter to hold inserts. The inserts are of steel or wood and are exchanged to effect changes in model density and center of gravity.

Figure 6 is a photograph of the model showing the details of construction.

The model was built to simulate a continuous oil boom constructed with a thin elastic skin inflated to a six-foot diameter and ballasted with water. Of course, the model more closely simulates a segmented oil boom in which the flexibility is concentrated at the joints.

The model parameters were chosen to be representative of a realistic oil boom configuration. However, the corresponding prototype is not necessarily a viable design.

The bending stiffness, *EI* and torsional rigidity, *GJ* of the oil boom prototype and model are shown in Table 1.

The effective bending stiffness and torsional rigidity of the model may be expressed as dimensionless quantities to eliminate absolute size as a parameter (see Equation (39):

$$L' = \frac{L}{D} = 84.1$$

$$S' = \frac{EI}{\rho g D^5} = 1.33$$

$$R' = \frac{GJ}{\rho g D^5} = 1.26$$

The model was tested in four conditions of ballast. These conditions are given as dimensionless quantities in Table 2.

Test Procedures

The oil boom model was tested in the Hydronautics Ship Model Basin in both calm water (steady state) and irregular long-crested waves. The model was towed to simulate ocean currents (relative to the oil boom mooring system) at nominal speeds of 0.25, 0.50, and 0.75 fps. Corresponding full scale currents are 0.66, 1.33, and 1.99 knots, respectively.

The boom mooring was symmetric in all tests, i.e., the line intersecting the two mooring points is at right angles to the current. The spacing between the mooring points on the towing bar was adjustable from 0 to 15 ft. A spacing of 8 ft. was chosen to represent a "fixed" mooring. This represents a condition where the full scale oil boom is moored to buoys or other fixed moorings which are spaced 160 ft. apart and symmetric to the flow. In other tests the mooring spacing was adjusted to simulate "drogue" mooring, i.e., where the oil boom is attached to drogue anchors that have no transverse resistance so that the mooring lines are parallel to the flow. Thus, in these tests, the spacings between the mooring points and between the boom ends are equal.

Drag (towing force) of the oil boom was measured by a variable reluctance type modular force gage upon which the towing bar was mounted. The gage capacity is 10 lb, but the forces involved in these tests ranged from only 0.1 to 1.0 lb. A low signal to noise ratio was a result of carriage induced vibrations in the towing bar and the low drag forces involved. However, by integrating the gage output over long time periods (50 sec) the drag component of the signal was effectively separated from the noise. These average (integrated) drag readings were repeated several times during each test and showed to be reliable to within ± 0.02 lb.

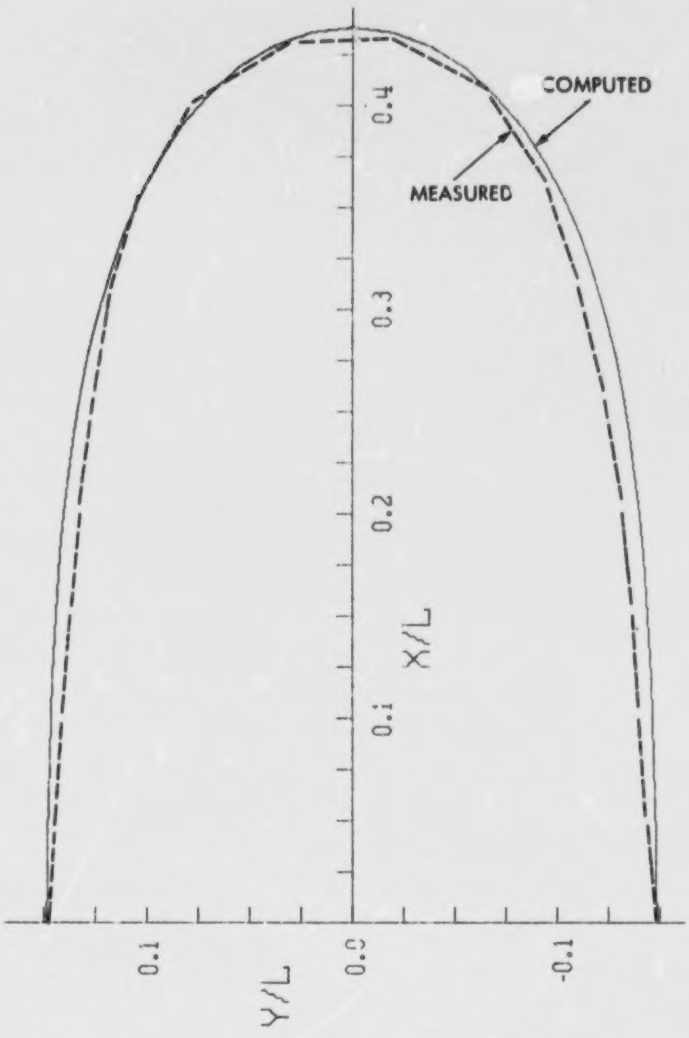


Figure 22. Comparison of computed and measured boom geometry, current 1.99 knots (Test 1, fixed mooring, model A, F_D = 0.236).

The shape of the oil boom in the horizontal plane was recorded photographically. The still camera was located about 11-ft. above the water surface. Typical photos of the boom in calm water and in waves are shown in Figure 8. The grid in these photos was made of cords at 2-ft. intervals and placed 1.79 ft. above the water level.

Irregular long-crested waves are generated by a wedge-shaped plunger at one end of the towing tank. Significant wave height and the spectrum of wave energy are controlled by a mechanically driven set of several sine-cosine potentiometers rotating at different frequencies and in random phase. The irregular signal generated by the system can be repeated by recycling to the same initial phases between potentiometers. The signal would ordinarily repeat only after about an hour in operation.

The tests in waves were conducted so that individual runs (in the same Sea State) were made over the same (similar, if not identical) irregular wave profile. The wave profile, with respect to a point on the mooring carriage, was measured by a sonic probe and recorded on a visicorder. The profile was recorded for about two minutes during the first run in each of the three significant wave heights. Records were not produced during succeeding runs.

Two movie cameras were used to record the motions of the oil boom when towed in head seas. (All tests in waves were conducted with current and waves running in the same direction). One movie camera was mounted overhead next to the still camera and the other was located about 5 ft. above the water and angled to give an oblique view of the water surface. The cameras were run simultaneously at a rate of 12 frames per second for about 55 seconds during each test.

Discussion of Test Results

Tests in Calm Water. The model was well behaved in the calm water tests. After some initial oscillations, due to the acceleration to the desired towing speed, the boom quickly assumed a steady shape. To simulate drogue mooring, the mooring spacing was adjusted while underway until an equilibrium (steady) shape was found in which the towing lines were parallel, i.e., the boom end spacing, S_B, equal to the mooring spacing, S_M.

After the boom had reached equilibrium, a photograph was made to record the shape in the horizontal, water plane (Figure 8). The profile seen in a photograph is not the true boom shape because of parallax errors.

Offsets were taken from the photographs and corrected for parallax to obtain the profiles (Figures 9 to 14). These are profiles of the oil boom centerline. The coordinate system for each profile was shifted so that the x-axis passed halfway between the boom ends and the y-axis passed through the point of one end. The oil boom profiles were not exactly symmetrical due to non-uniformities in the model construction and towing lines.

The measured towing conditions for each test are given in Table 3 in non-dimensional form:

Froude number, $F_D = \dfrac{V}{\sqrt{gL}}$

Mooring spacing, S_M/L

Boom spacing, S_B/L

Towing line length, T/L

There does not appear to be any significant changes in the model profiles with respect to the four geometries *(A, B, C and D)*. Change in the vertical center of gravity (Table 2) would not be expected to affect the towing behavior in calm water. A change in model density might be expected to have an effect due to the increase in drag with greater submergence. However, this effect is not readily apparent in the figures. Note that the change in draft between model configurations is about 10 per cent. A 5 per cent increase in Froude number can be expected to change the drag by the same amount as a 10 per cent increase in draft.

Significant changes in the boom profile arise from the towing speed (Froude number) and the lateral spacing between the mooring points. These changes are obvious in the figures and follow trends that would normally be expected.

Calm water drag data are presented in Figure 15. The drag coefficient is defined by

$$C_D = \frac{D}{\frac{1}{2}\rho V^2 HL} \tag{41}$$

where

D = drag, lb.

V = current velocity, fps.

H = draft, ft.

L = boom length, ft.

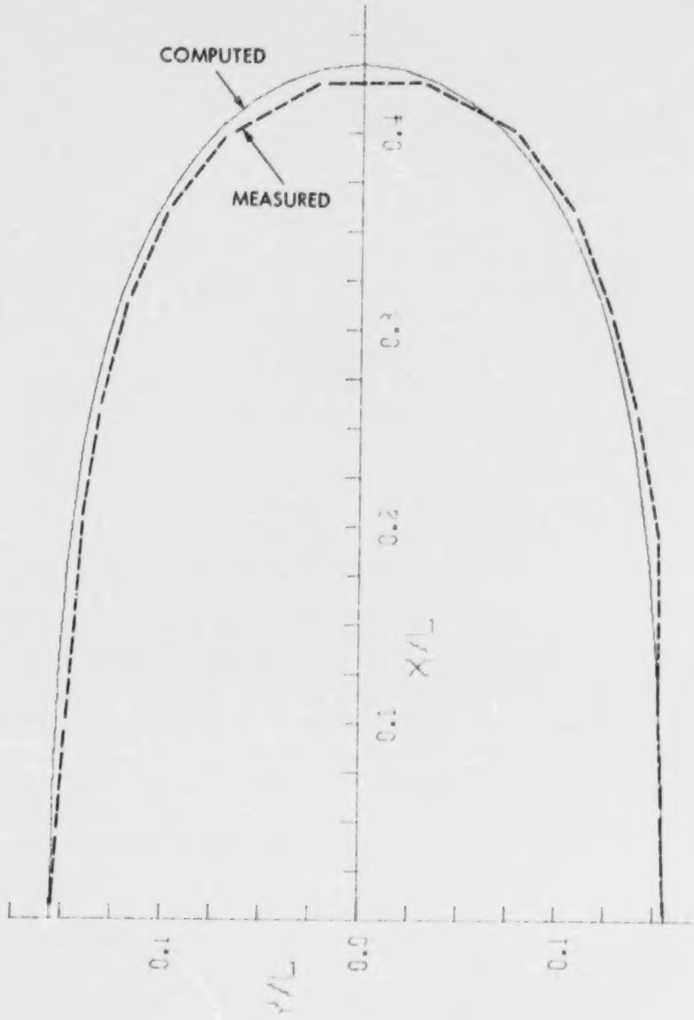


Figure 23. Comparison of computed and measured boom geometry, current 1.33 knots (Test 2, fixed mooring, model A, F_D = 0.157).

The drag data are shown as a function of mooring spacing, S_M. The mooring conditions (fixed or drogue) and Froude Numbers are indicated by the data point symbols. No significant effects due to Froude Number or mooring conditions are apparent from these data. The model configurations are not indicated in this figure; however, they also show no effect. A dashed line is shown to indicate the tendency of the drag coefficient to increase as mooring spacing increases, as should be expected.

Tests in Waves. Irregular waves were generated in the towing tank in such a way that their spectral density $S(\omega)$ would simulate the spectrum given by Pierson-Moskowitz.[6] This spectrum may be expressed by

$$S(\omega) = \frac{A}{\omega^5} \cdot e^{-\frac{B}{\omega^4}} \qquad (42)$$

where

$A = 8.39, \text{ft}^2/\text{sec}^4$

$B = 33.56/(H1/3)^2$

ω = frequency, rad/sec, and

$H1/3$ = significant wave height, ft.

The "significant" value in this discussion is defined as the average of the highest one-third values of the parameter in question.

The wave records from the model tests were treated statistically to find the spectral density as a function of wave frequency ω and the significant wave height (from crest to trough). Three different "seas" were generated and correspond, nominally to Sea States 3, 4 and 5. Each different sea was used for tests at a different current (Table 4). The spectral densities are shown in Figures 16, 17 and 18 along with the Pierson-Moskowitz spectrum of the same significant height. The wave data shows quite good agreement with the desired spectrum. However, it should be noted that the data points represent the wave energy over the frequency band between the data points. If data points are calculated for more narrow frequency bands they will show that the wave energy is actually concentrated at the discrete frequencies in which energy is supplied to the wave maker.

The model behavior in waves was similar to behavior in calm water. A mean profile similar to those in calm water tests was assumed after starting the carriage, but the segments oscillated about this mean profile in response to the action of the waves. It is interesting to note that the boom segments have greater motions at zero speed (no towing forces). The tension in the boom when towing has a stabilizing influence.

In Sea State 3 the boom segments did not submerge. Water occasionally washed over segments of the boom in Sea State 4 and did so frequently in Sea State 5. The middle segment was totally submerged at least half of the time during tests in the highest sea state. At no time was a segment seen to lift out of the water.

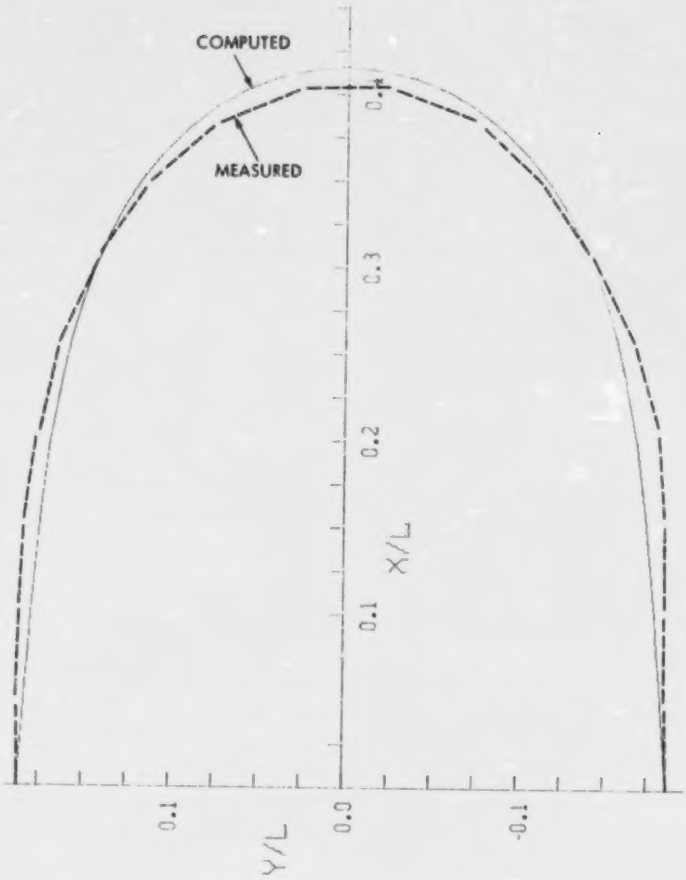


Figure 24. Comparison of computed and measured boom geometry, current 0.66 knots (Test 3, fixed mooring, model A, F_D = 0.075).

The drag data for tests in waves are presented in Figure 15 along with the data from calm water tests. These data show that the drag is significantly increased by the presence of waves. In all other respects the drag in waves is similar to the drag in calm water.

Data were taken from frame-by-frame analysis of motion pictures to determine the boom motions in terms of angles of roll γ pitch β and yaw α between adjoining segments (Figures 19, 20 and 21). The significant values of the peak to peak angular motions are given in these figures. It should be noted that these angles represent the average angles for a complete segment length and should be divided by the segment length to get an angle per unit length or curvature.

The data points in Figures 19, 20 and 21 are accompanied by notation which indicates the boom model *(A, B, C, or D)* the mooring spacing, in model scale, and, the adjoining boom segments where No. 1 is the end segment and No. 10 is the middle segment. The angular motions are plotted as functions of the significant wave height, in prototype scale.

Model configuration, i.e., center of gravity and weight, and mooring spacing had no discernable effect on the motions that were measured. The affect of wave height, however, is evident and follows expected trends, e.g., higher waves cause greater motions.

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TABLE 1. OIL BOOM CHARACTERISTICS

	Model ($\lambda = 20$)	Prototype
L, ft	25.25	505.0
D, ft	0.30	6.0
EI, lb-in.^{2}	29.0*	95.6×10^6
GJ, lb-in.^{2}	27.4*	90.5×10^6

* Note: effective value

The values of EI and GJ are given as effective values for the model, i.e., the stiffness of the joint is adjusted by the relative lengths of the joint and the model segment to obtain the stiffness equivalent to a model boom having continuous flexibility.

TABLE 2. MODEL BALLAST CONDITIONS

Model Designation	A	B	C	D
$4W/\rho g \pi L D^2$	0.700	0.700	0.625	0.625
CG/D	0.096	0.049	0.055	0.107
H/D	0.742	0.742	0.672	0.672
A_F/LD	0.683	0.683	0.608	0.608

where

W = model weight, lb

CG = distance from boom axis to center of gravity, ft

H = draft, ft

A_F = frontal area, ft^2 (see Figure 7)

TABLE 4. CURRENT AND WAVES USED IN MODEL TESTS

Sea State	3	4	5
Significant wave height $\overline{H}_{1/3}$, ft.	4.91	6.80	13.33
Current V_k, knots*	0.67	1.33	1.99

* given to prototype scale

TABLE 5. MEASURED AND COMPUTED DRAG COEFFICIENTS FOR MODEL A

Test No.	Current (Knots)	Froude No.	Drag Coefficients	
			Measured	Computed
1	1.33	0.236	0.215	0.214
2	0.66	0.157	0.240	0.221
3	1.99	0.750	0.275	0.250

APPENDIX III - SYMBOL DEFINITION

A	Effective structural cross-sectional area of boom
A_F	Frontal area of submerged portion of boom
CA	Angular (α) mooring spring constant
C_D	Drag Coefficient
CG	Distance from boom axis to center of gravity
CX	X direction mooring spring constant
CY	Y direction mooring spring constant
DA	Angular (α) mooring damping coefficient
DX	X direction mooring damping coefficient
DY	Y direction mooring damping coefficient
E	Modulus of elasticity
F	A characteristic applied force
F_b	Buoyant force
F_c	Current force
F_w	Wind force
G	Shear modulus of elasticity
g	Acceleration of gravity
H	Draft of boom
h	Wave height
h'	Non-dimensional wave height
I	Boom section moment of inertia
J	Boom section polar moment of inertia
K	A function of the load distribution
L	Total boom length; a characteristic length
L'	Non-dimensional length
φ	One half length of boom element (Figure 1)
M	Bending moment on end of boom element (Figure 1)
MA	Angular (α) mooring effective mass
MX	X direction mooring effective mass
MY	Ydirection mooring effective mass
R'	Non-dimensional torsional rigidity
S	Shear on end of boom element (Figure 1)
S'	Non-dimensional stiffness
S_B	Boom end spacing
SL	Distributed shear along boom element
S_M	Mooring spacing
$S(\omega)$	Spectral wave density function
T	Tension on end of boom element; towing line length
TL	Distributed tension along boom element (Figure 1)
Δt	Time increment used in dynamic calculations
V	A characteristic velocity
V'_c	Non-dimensional current velocity
V_k	Current velocity (knots)
V_w'	Non-dimensional wind velocity
W	Model weight
x	Reference streamwise coordinate of end of a boom element (Fig. 1)
y	Reference coordinate normal to streamwise direction of end of a boom element (Fig. 1)

α	Angle between stream direction and end of a boom element
$\Delta\alpha$	Angular deflection of a boom element (Figure 1)
γ	Linear deflection of a boom element (Figure 1)
δ	A characteristic deflection
δ_b	Deflection due to buoyant forces
δ_c	Deflection due to current forces
δ_w	Deflection due to wind forces
τ	Scale ratio
ρ	Axial elongation of boom element (Figure 1)
ρ_A	Density of air
ρ_w	Density of water
ω	wave frequency

Subscripts

i	i'th element on boom
1	first element of boom
k	last element of boom
m	model
p	prototype

TABLE 3. CALM WATER TOWING CONDITIONS

Figure	Mooring	Test	FD	SM/L	SB/L	T/L	CD
4	FIXED	1	0.2360	0.3168	0.2966	0.2976	.215
		18	0.2360	0.3168	0.2991	0.3067	.215
		29	0.2410	0.3168	0.3070	0.2950	.205
		41	0.2480	0.3168	0.2951	0.3054	.219
5	FIXED	2	0.1570	0.3168	0.3106	0.2662	.24
		15	0.1530	0.3168	0.3020	0.3155	.28
		27	0.1670	0.3168	0.3166	0.2645	.225
		39	0.1700	0.3168	0.3109	0.3036	.215
6	FIXED	3	0.0750	0.3168	0.3739	0.2551	.275
		14	0.0700	0.3168	0.4364	0.2506	.137
		26	0.0800	0.3168	0.4125	0.2579	.236
		37	0.0860	0.3168	0.3634	0.2593	.149
7	DROGUE	6	0.2280	0.1782	0.1874	0.2891	.164
		17	0.2370	0.2110	0.2145	0.2887	.17
		30	0.2400	0.2178	0.2239	0.2854	.172
		42	0.2460	0.2110	0.2089	0.3010	.185
8	DROGUE	5	0.1480	0.3037	0.3066	0.2949	.218
		16	0.1510	0.3037	0.2634	0.2888	.228
		28	0.1650	0.3037	0.3110	0.2941	.21
		40	0.1640	0.2839	0.2878	0.2867	.175
9	DROGUE	4	0.0700	0.5279	0.6308	0.2872	.260
		13	0.0720	0.4356	0.4781	0.2705	.115
		25	0.0810	0.4784	0.5159	0.2629	.315
		38	0.0830	0.4819	0.5188	0.2615	.097

S_m = Mooring Spacing (tow line, spacing as fixed to tow carriage)

S_b = Boom end spacing (spacing of ends of boom as attached tow lines)

L = Boom length

T = Towline length

F = Froude Number

C_d = Drag coefficient

Oil Pollution Control On The Buffalo River

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Abstract

Cornell Aeronautical Laboratory, Inc. is performing research and development for the City of Buffalo, to formulate practical techniques for controlling river oil pollution. The program is supported in part by a grant from the Federal Water Pollution Control Administration.

Summarizing progress to date, the paper discusses the two main systems developed: the upper river system (surface oil booms) and the lower river system (underwater air barrier). The basic design of the air barrier is discussed, along with the results of laboratory and field testing. The sampling and analysis phase is summarized, in addition to oil retrieval and the use of surface chemical displacing compounds.

For many years, the Buffalo River has been plagued by oily discharges from municipal and industrial sources. These discharges have also contaminated the waters of the Buffalo harbor and the Niagara River. In addition to continuous discharge, accidental spillage and clandestine disposal have occurred in recent years. The City of Buffalo received a demonstration grant from the Federal Water Pollution Control Administration to formulate practical techniques and tools for controlling river oil pollution. As subcontractor to the City, Cornell Aeronautical Laboratory (CAL) is performing the research and development for the program.

The program includes many related areas of development such as techniques to analyze oil samples to identify their source, methods for sampling oil to determine its concentration in the river, and methods for detecting and trapping oil in sewer systems. In the present paper, the discussion and results will be limited to those aspects of the program that pertain to the containment and distribution of oil in the river.

Description of Buffalo River and Containment Systems

The Buffalo River (Figure 1) has a drainage basin of approximately 450 square miles. The portion of the river we are concerned with is a 5-½ mile stretch from the mouth upstream to where Cazenovia Creek meets the river. This section of the river, except for the last half mile, is part of a federal dredging project by the Army Corps of Engineers. The average channel depth is about 25 feet at mean water level; the average width of the river is about 275 feet. Dividing this section of the river in half, the upper half comprises an industrial complex, including an oil refinery, a steel mill, a chemical plant, and a coke company. The lower half is dominated by grain facilities and light industry.

The hydraulic properties of the river can change drastically during the yearly seasons. Beginning in winter, the river section from Bailey Avenue upstream to the headwaters freezes to a depth of one to two feet. Because of thermal discharges, the remainder of the river is usually free of ice, except for skim ice out to the mouth. At spring thaw, the river flow reaches about 40,000 cfs, producing peak surface flows of about 5 feet per second at the mouth. After peak runoff, the river becomes relatively quiescent, as evidenced by a 30-year average annual flow of only 500 cfs.

Immediately after the spring runoff, oil slicks appear in the lower river area, presumably as a result of scouring of the bottom muds and shoreline, and the release of build-ups of oil pools under the ice. In the summer and early fall, the prevailing southwest wind transports surface oil into the residential areas of Bailey Avenue on the

Table 1. Results Summary

SURFACE VELOCITY (ft/sec)	PRESSURE (psig)	ORIFICE (mm)	ORIFICE SPACING (ft)
1.6	20	2	1
1.5	50	2	2
1.1	20	2	2
1.0	50	1	1

Buffalo River and Cazenovia Creek. This wind also prevents surface oil from passing downstream to the mouth and much of the oil eventually pools in the industrial area.

It is evident that two containment systems are required: an upper river system to prevent transport of oil upstream in summer and fall, and a lower river system to prevent loss of oil at the mouth. The remainder of this section describes the development of these two systems.

Upper River System: The containment problem of the upper river area is relatively simple to solve by installing surface oil booms above the high point of navigation. One major problem, however, is to protect these booms from debris and the effects of high flow caused by an occasional heavy rain. Several different types of surface oil booms and methods of installation are currently being investigated. The present installation consists of two boom assemblies placed across the Buffalo River and Cazenovia Creek at Bailey Avenue. Figure 2 shows a typical boom assembly in place across Cazenovia Creek. Because of ice, these booms must be removed in late fall and reinstalled immediately after the spring thaw. Debris trapped by these booms is removed by a clamshell crane from the Bailey Avenue Bridge.

Lower River System: Since the river is open to navigation, lake tankers in the lower river present a problem. To solve this problem, an underwater air barrier was developed by CAL to allow the passage of ships and still retain oil. The air barrier consists of a perforated pipe placed beneath the surface of the water through which air is ejected, as shown in Figure 3. The ejected air breaks up into bubbles which, being buoyant, rise. The rising bubbles impart momentum to the surrounding water, producing a vertical current of water and air. At the water surface, the rising column of water creates a flow along the surface on

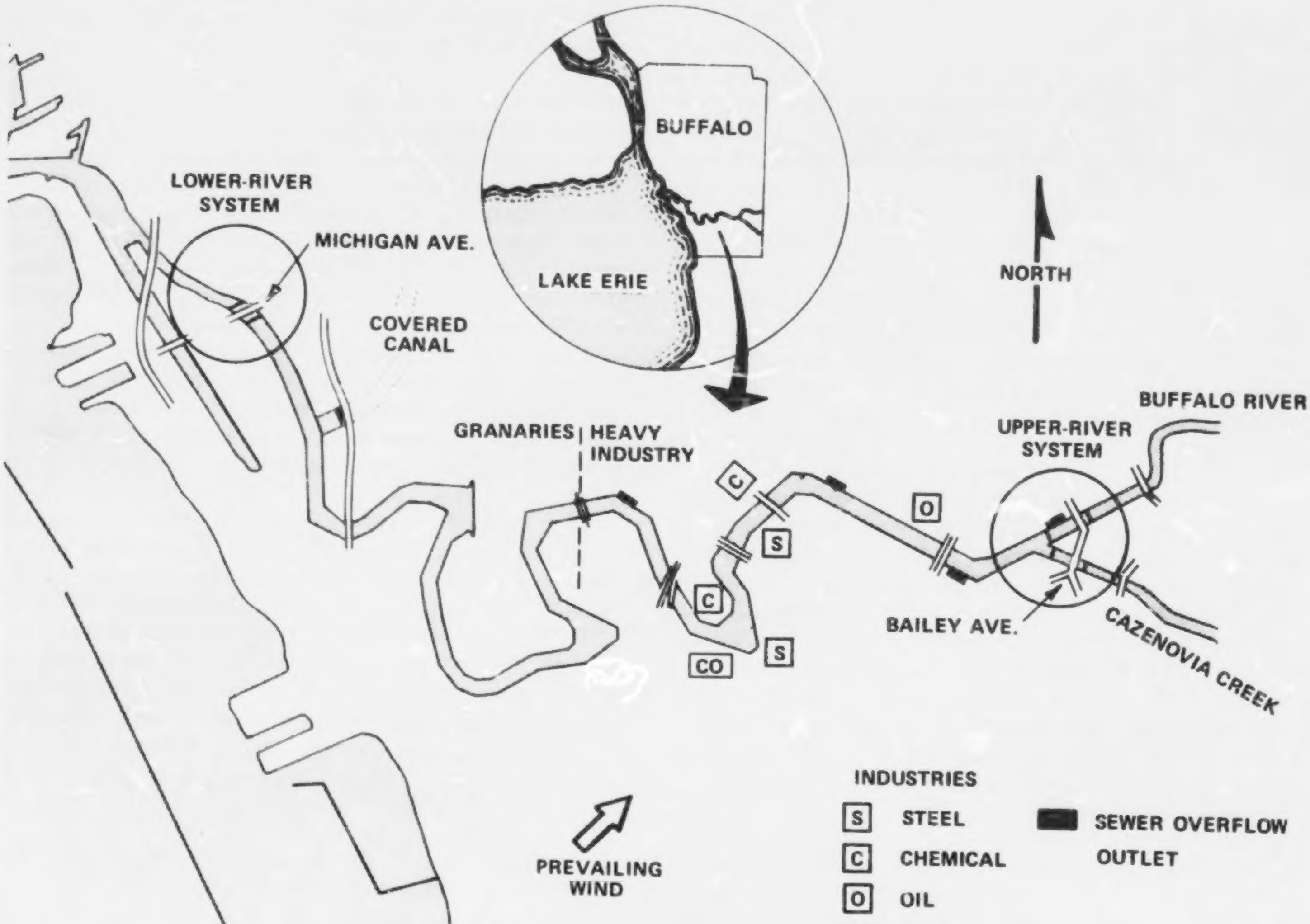

BUFFALO
LAKE ERIE
LOWER-RIVER SYSTEM
MICHIGAN AVE.
COVERED CANAL
NORTH
BUFFALO RIVER
UPPER-RIVER SYSTEM
GRANARIES
HEAVY INDUSTRY
C
S
O
C
S
CO
S
BAILEY AVE.
CAZENOVIA CREEK
PREVAILING WIND
INDUSTRIES
S STEEL
C CHEMICAL
O OIL
CO COKE
■ SEWER OVERFLOW OUTLET

Figure 1. Map of Buffalo River area concerned with the study.

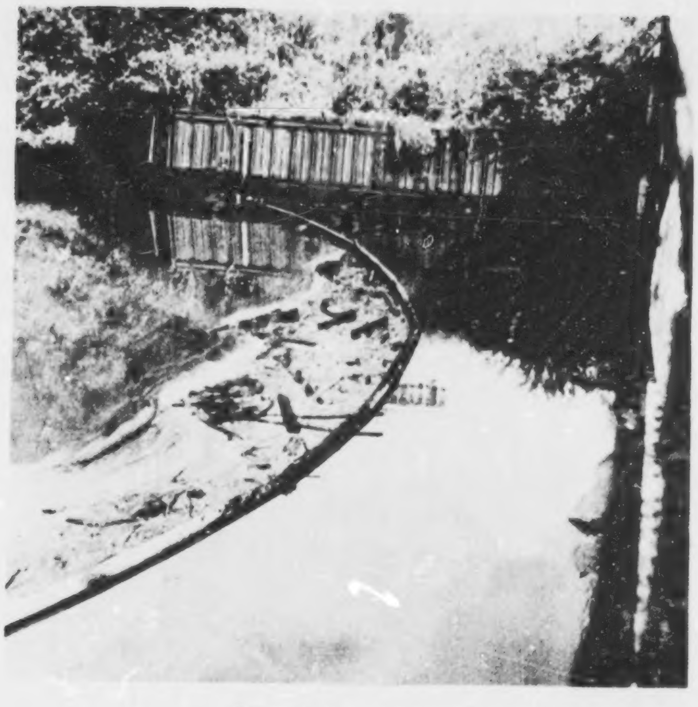


Figure 2. Boom assembly.

each side of the rising column. This surface current can be used to restrain the flow of surface material.

Air barriers are not new; however, very little quantitative data on the operation of these devices are available, especially for containment of oil. Most information is derived from tests of the devices as breakwaters. Although some of this information is useful, data are still lacking on operation of air barriers in deep water and under flowing water conditions.

The development of the air barrier was initiated with laboratory studies to determine the design parameters for an air barrier system. Based on these studies, a barrier was designed and installed in the Buffalo River. A program was then initiated to test the effectiveness of the device in a river current.

Laboratory Studies: To investigate the design parameters for an air barrier system, experiments were conducted in a swimming pool test facility at CAL. The tank is 60 feet long, 15 feet wide, and 15 feet deep. Several single- and multiple-nozzle configurations were tested while pressure, nozzle size, depth, and nozzle spacing were varied. In these tests the resultant surface velocity was measured. The approach was to determine the factors that maximize the surface velocity under stagnant conditions, and assume that this velocity could be used to counteract an equal surface current in the real case. The general results of these laboratory tests are as follows: the surface velocity depends on critical depth; it is independent of nozzle orientation and it is increased more by an increase in air volume flow rate than by increased supply pressure.

The tests also included a prototype of the barrier contemplated for installation in the river. The prototype (Figure 4) consisted of a 14-foot length of 3-inch diameter polyethylene pipe drilled to provide for changes in nozzle size and spacing. Surface velocities were measured with an OTT propeller-type current meter near the water surface. Because of results obtained in earlier tests, nozzle orifices were limited to 1 and 2 mm. The tests were conducted with a 5-hp compressor capable of delivering air at a rate of 27 cfm at 100 psig. A summary of the results is shown in Table 1, which lists the maximum surface velocities possible for the various nozzle configurations and the above compressor.

Barrier Design: Based on these results, a barrier was designed and installed for testing near the mouth of the Buffalo River. The barrier was designed, as in the laboratory case, to provide for changes in nozzle spacing and size. Figure 5 is an aerial view of the site with the barrier position superimposed at an angle of 84° to the river current. The maximum river depth at this site is about 28 feet at mean water level, and the distance across the surface of the water is 220 feet. The barrier is 250 feet long and follows the contour of the river bottom. On each side of the river, the barrier terminates against a vertical wall to prevent end losses of oil. The river bottom at this site was determined to be hard packed clay, which simplified some design considerations such as the problem of the barrier burying itself in silt. To provide sufficient air volume over a wide range of pressures, two 600-cfm, 150-hp, rotary, electric air compressors were used.

To reduce the cost of raising and lowering the barrier for changing nozzles and other maintenance, the system was designed to be floated to the water surface. Figure 6 shows a short section of the barrier; the center pipe carries the compressed air and the outer pipes are filled with water. When the barrier is to be raised, the air supply is used to purge the water from the outer pipes. With all three pipes filled with air, the system will float. Drag cables were installed on either side of the barrier and anchored to the shore to prevent possible motion of the barrier during heavy runoff. The entire system was weighted with concrete blocks.

River Testing: On completion of the installation of the barrier, a program was initiated to test the effectiveness of the device in a river current. It was not possible to make detailed velocity surveys over the surface of the river due to river traffic and lack of a suitable measuring platform. Therefore, measurements of velocity were limited to points directly below the Michigan Avenue Bridge. Figure 7 shows the barrier in operation with the

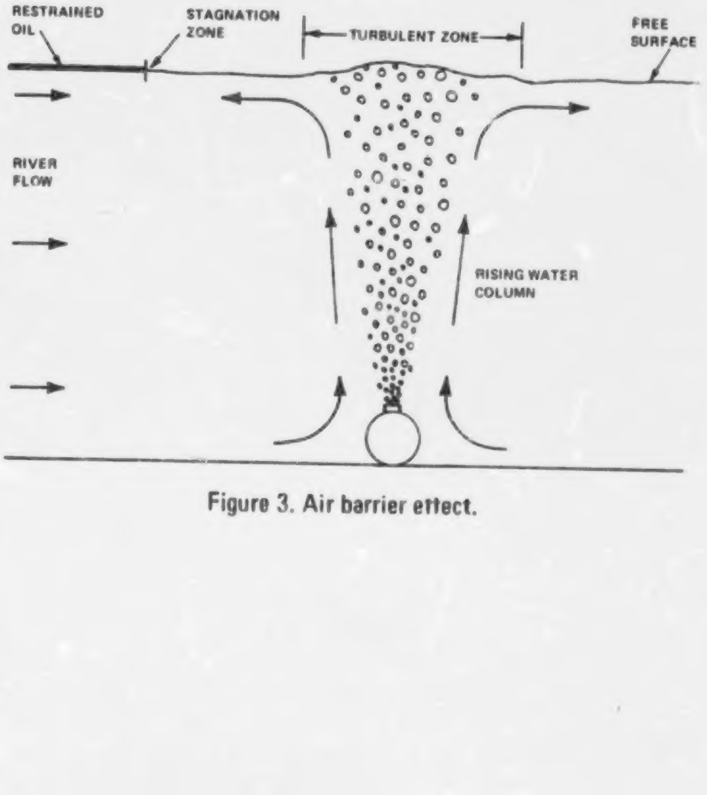


Figure 3. Air barrier effect.

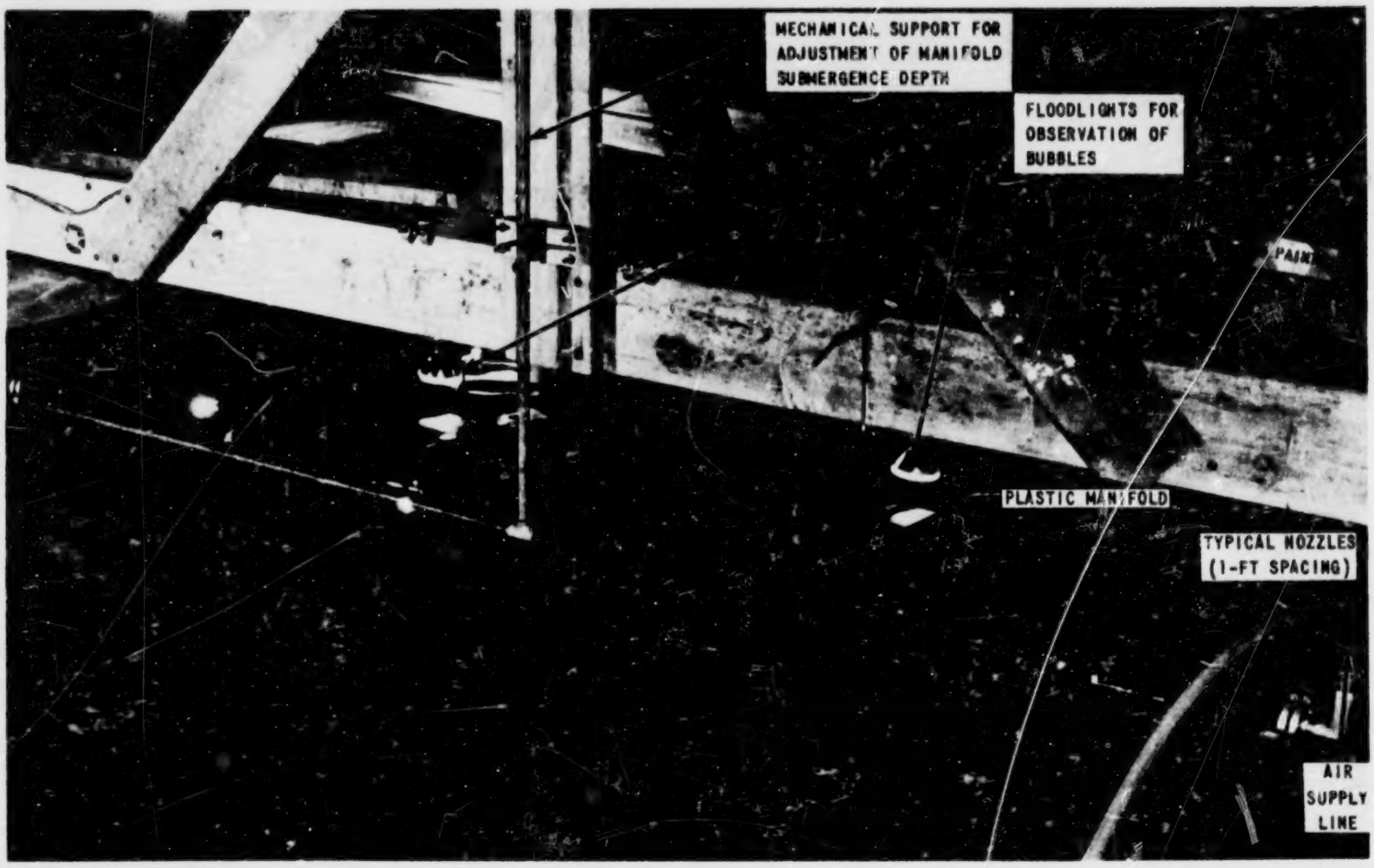

MECHANICAL SUPPORT FOR ADJUSTMENT OF MANIFOLD SUBMERGENCE DEPTH
FLOODLIGHTS FOR OBSERVATION OF BUBBLES
PLASTIC MANIFOLD
TYPICAL NOZZLES (1-FT SPACING)
AIR SUPPLY LINE

Figure 4. Test configuration of pneumatic barrier prototype in water tank.

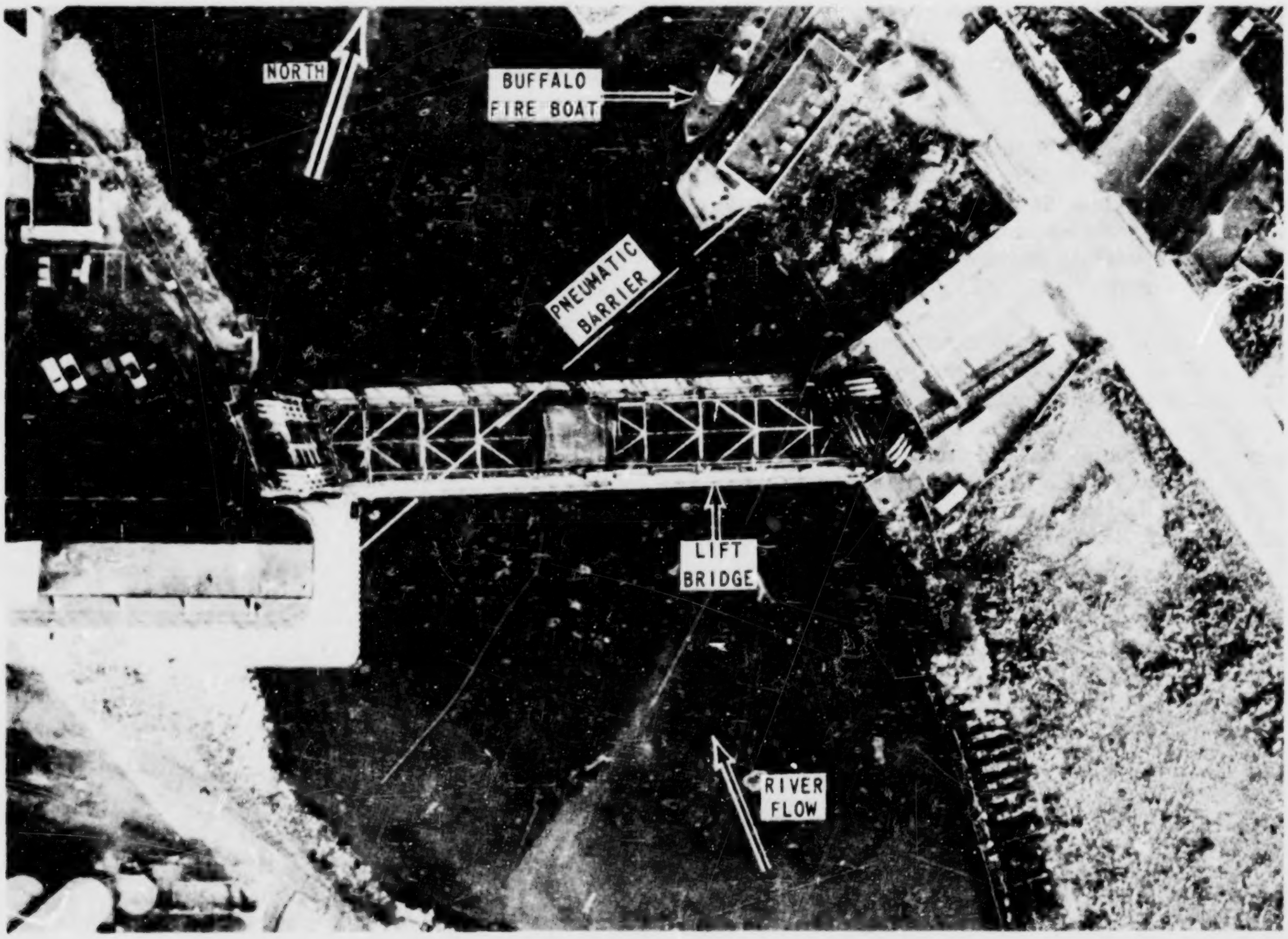

NORTH
BUFFALO FIRE BOAT
PNEUMATIC BARRIER
LIFT BRIDGE
RIVER FLOW

Figure 5. Aerial view of pneumatic barrier location.

Michigan Avenue Bridge in the background. A current meter was suspended from the bridge into the water, but out of the influence of the barrier. River currents observed during the testing period were mostly 1 fps or less. Some data were obtained for velocities of 1.5-1.75 fps; however, these conditions did not persist long enough for a series of measurements to be taken.

In addition to surface velocity, the relationship of the zone of turbulence to the retained oil slick was measured to make a qualitative evaluation of barrier effectiveness. When the flow in the river is zero, the distance between the turbulent zone of the barrier and the oil slick is at a maximum (Figure 3). As the river current increases, the oil slick, the rising air-water column, and hence, the turbulent zone at the surface are displaced downstream.

One form of failure results when the system is no longer able to generate a continuous curtain of air so that a "wash-out" of the bubble pattern occurs. This type of failure was found to be eliminated for the river currents tested by maintaining a sufficient supply pressure and, hence, flow rate from each nozzle. For all currents observed, a minimum supply pressure of 30 psig was sufficient to prevent failure by "wash-out."

A second form of barrier failure is expected to occur when the distance between the turbulent zone of the barrier and the oil slick becomes smaller, i.e., when the river current is sufficiently high to compress the oil slick toward the turbulent zone. In this case, oil may be trapped by vortices that exist on the edge of the zone of turbulence, and the oil may be drawn under the water surface and reappear on the downstream side. The vortices appear to be generated as a result of the interaction of adjacent air-water columns. This effect was demonstrated through separate tests in the laboratory, but could not be absolutely established in the river under test conditions.

Unfortunately, full testing of the air barrier has been limited during the summer and fall by 1) an absence of large quantities of oil at the site, 2) the buildup and loss of oil slicks caused by the change in the direction of the river current several times daily, and 3) the absence of river currents strong enough for extensive study of barrier breakdown. In spite of these limitations, however, evaluation of the barrier has shown that the present nozzle configuration (2-mm nozzles at 2-feet spacing) will retain thin layers of surface oil in river currents of 1.5 feet per second when the air supply is at 600 cfm at 50 psig. To provide data on higher velocities, tests are planned for the spring thaw, when surface velocities reach about 5 fps.

Sampling and Distribution of Oil in the River

To aid in the selection of containment and oil retrieval systems, a sampling and analysis phase was initiated to determine distribution and fate of the oil discharged into the river. This work has required development of special sampling techniques to determine the oil load in the river, the results of which have changed some of the original concepts of oil pollution problems in the river. The following sections describe some results of sampling during the past summer and early fall.

Surface Sampling: Figure 8 illustrates the hoop sampling method which has been devised to confine, concentrate, and quantitatively recover surface oil films. In this method a plastic hoop whose inside surface is coated with a surface-active agent, is deployed onto the water surface to be sampled. The surface-active agent (sorbitan monooleate, a non-toxic material) spreads from the inner surface of the hoop, compressing the surface film into a small area. Filter paper is then used to blot the concentrated film from the surface. By preweighing the filter paper, the sample weight recovered (per unit area) can be directly estimated simply by reweighing the filter papers after use. Using this method, we have determined the equilibrium surface load during the summer period to be 100-150 gallons of oil.

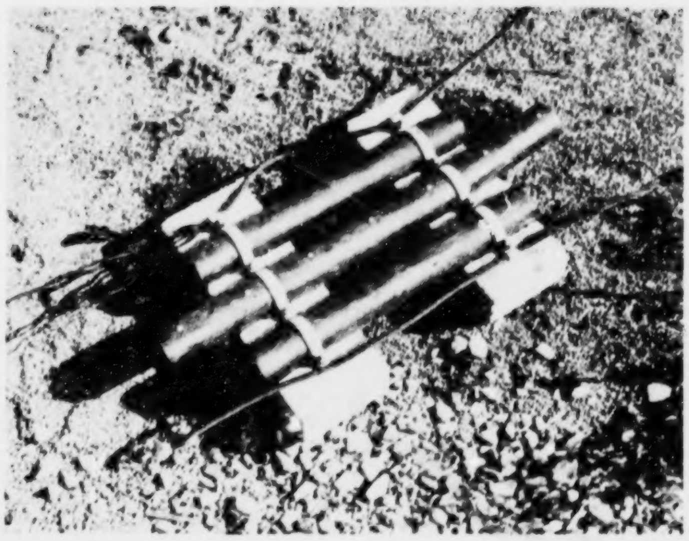


Figure 6. Barrier mockup.

Bottom Samples: Periodic bottom samples taken along the length of the river have consistently indicated that the bottom muds contain 1 - 3.5 percent oil, with the highest concentrations in the industrial section.

Shore Sampling: We observed large amounts of oil in the upper river compared to a small amount at the site of the air barrier near the mouth of the river. This observation led us to postulate that oil was being lost to the shoreline in its transit down the river. To sample this shoreline deposition, ten aluminum strips were wrapped with muslin cloth and attached to each of five plywood panels. The panels were then placed along the river so that the strips were submerged, as shown in Figure 9. Each week a strip was removed and the oil content of the

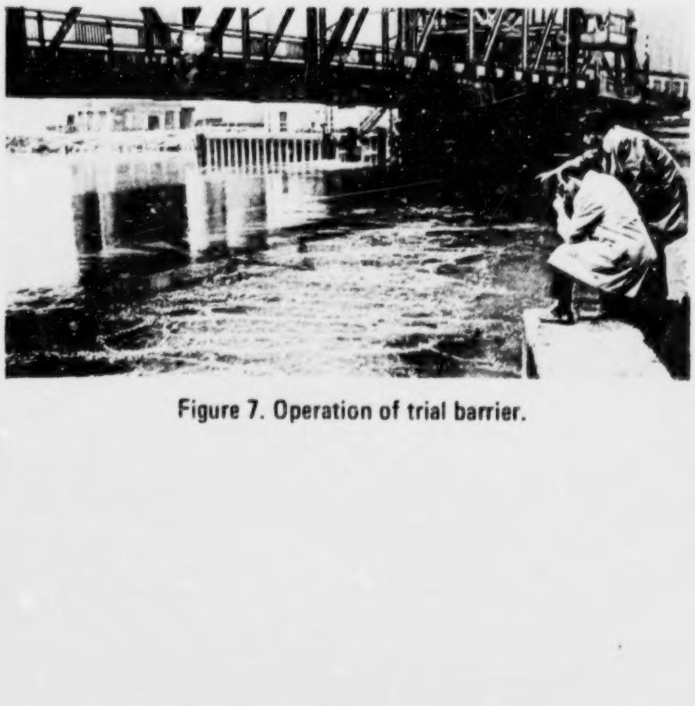
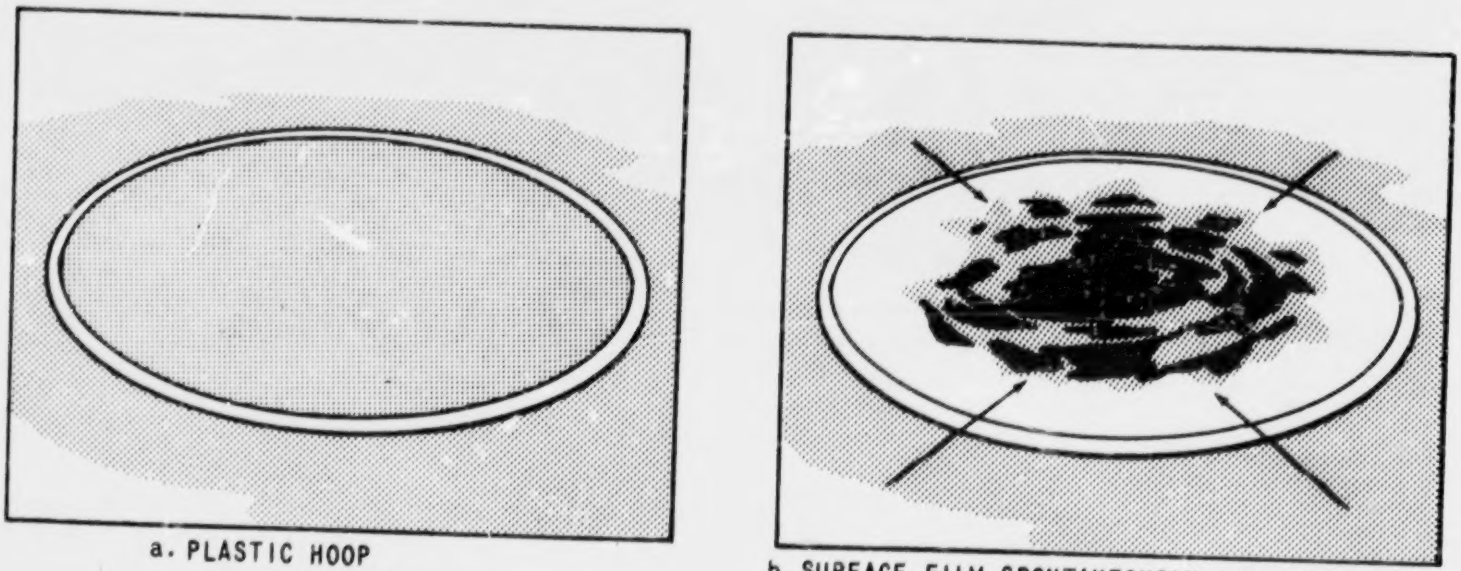
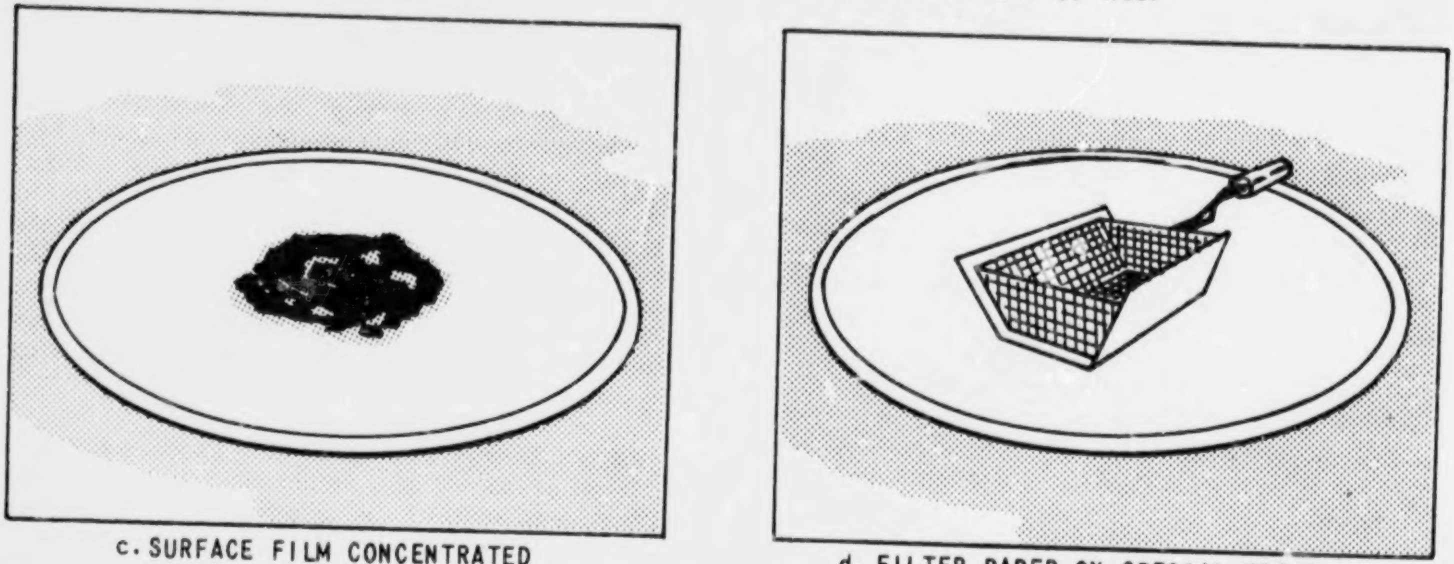


Figure 7. Operation of trial barrier.



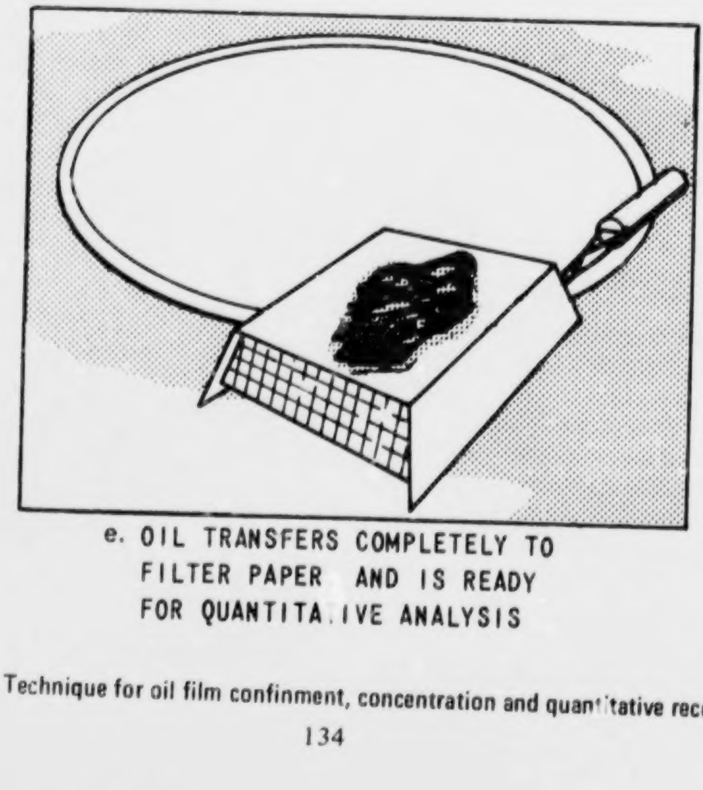
a. PLASTIC HOOP CONFINING KNOWN AREA OF SURFACE FILM

b. SURFACE FILM SPONTANEOUSLY COMPRESSED BY SURFACE-ACTIVE AGENT SPREADING FROM INNER PERIPHERY OF HOOP



c. SURFACE FILM CONCENTRATED INTO THICK POOL AT HOOP CENTER

d. FILTER PAPER ON SPECIAL FRAME IS TOUCHED TO OIL PATCH



e. OIL TRANSFERS COMPLETELY TO FILTER PAPER AND IS READY FOR QUANTITATIVE ANALYSIS

Figure 8. Technique for oil film confinment, concentration and quantitative recovery.

muslin was determined. With this method, we have concluded that 100 to 500 gallons of oil per day could be deposited to the shore in the 2.1-mile length of the industrial area. Figure 10 shows a plot of a four-week total oil deposition per foot of shoreline at several positions along the river. This curve illustrates that a "natural surface barrier" has been formed by the physical features of the river, namely, the "S" curves and turns, the reverse flow caused by the rising and falling lake level, and the predominant southwest wind. This "natural barrier" phenomenon explains the unexpected absence of large quantities of surface oil at the air barrier site near the mouth.

Bulk Water Samples: Bulk water samples also were taken at strategic points along the river with a Kemmerer bottle. These samples were collected mid-stream at mid-depth and were analyzed by hexane extraction. The results show a parts per million content from 1 to 11, with an average of about 5 ppm. Taking this average and using the average annual flow of 500 cfs, or about 300 MGD, approximately 1500 gallons of oil per day flow out the mouth of the river. Combining this approximation with the estimate of amount of oil deposited on the shore, 1600 to 2000 gallons of oil are removed from the river each day. This amount compares with 1700 gallons[1] discharged by the three largest industrial sources on the river. By estimating average depth and width of the river from the mouth upstream to Bailey Avenue, the volume of water present in this portion is approximately 1000 million gallons. This value, along with the average oil content of 5 ppm, shows the equilibrium bulk water oil load to be about 5000 gallons. Comparing this value with the surface oil load, the ratio of emulsified oil to surface oil is 33 to 1.

Data collection of this type is to continue during the coming winter months to establish the changes, if any, in oil movement and distribution at reduced temperatures and when ice cover conditions exist in the upper river.

Oil Retrieval

With the data thus far accumulated on oil concentrations and distributions, oil retrieval systems are being investigated. Except for spillage, the data indicate that the thickness of surface oil slicks available for retrieval range from 0.1 to 2.5 microns. With the oil booms in place on the upper river, this oil is confined mostly to the 2.1-mile industrial area. It is evident that the efficiency of any retrieval system can be maximized if the surface oil can be effectively concentrated. Surface chemical displacing compounds such as sorbitan monooleate discussed previously appear to have widespread application for concentrating or otherwise controlling oil slick size and motion. These compounds are innocuous surface-active agents which compete with the oil for a place at the interface, and in so doing, efficiently guide the oil away from the point of application and thicken the slicks into more readily recoverable pools. We have experimented with these compounds on the Buffalo River and have met with some success.

Currently envisioned applications of these compounds include: 1) driving oil accumulations from inaccessible locations, such as around piers and bridge pilings (where they are almost impossible to collect and represent a fire hazard) into the main stream for boom or skimmer collection, 2) guiding oil from shoreline and upstream locations to the collecting booms, and 3) thickening and containing the oil slicks at the skimmer locations to increase the skimmer efficiency.

Figure 9. Test panel.

Present plans call for the design of a retrieval system which will be tested in the spring of 1970. This will be combined with efforts to increase containment of surface oil such as encircling various outfalls or possibly moving the air barrier to a new site upstream where more oil would be accumulated.

Summary

Because of physical features and wide changes in weather conditions, the Buffalo River requires oil containment systems at upstream and downstream locations. Surface oil booms have proved effective in stopping surface oil from moving upstream and yet withstanding

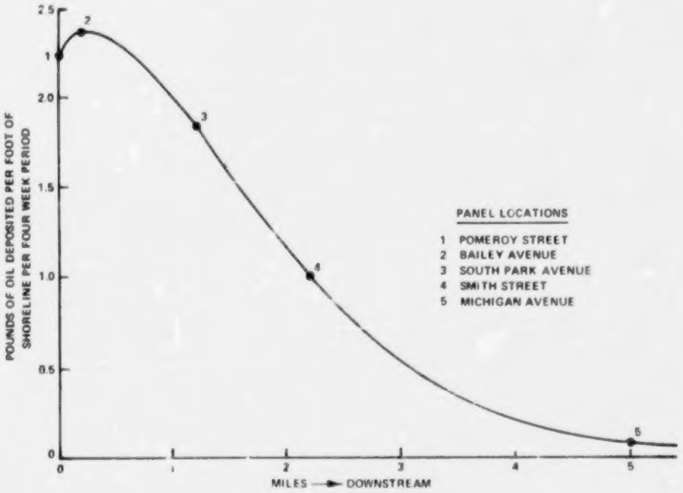


Figure 10. Shoreline oil deposition illustrating "natural surface barrier."

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[1] Superior numbers refer to literature references at conclusion of text.

high flow during rainy periods. An air barrier has been developed that will restrain surface oil under typical river flow conditions but requires further testing under high flow. River oil sampling has shown that much of the oil discharged to the river exists in the bulk of the water. Most of the surface oil that is present is eventually deposited to the shoreline but may be scoured loose during spring thaw. Retrieval systems for surface oil are being investigated along with surface-active agents to aid in concentrating the oil.

Acknowledgment

The author wishes to acknowledge the efforts of Messrs. A. Sowyrda and J.M. Grace of CAL, who designed and tested the air barrier and of Dr. R.E. Baier, also of CAL, who developed the surface sampling techniques. Mr. T.J. Lyons, Associate Engineer, City of Buffalo, Department of Public Works, supervised the installation of the containment systems.

Reference

[1] "Summary Report on Pollution of the Niagara River to the International Joint Commission," prepared by Lakes Erie-Ontario Advisory Board to the International Joint Commission on Control of Pollution Boundary Waters, October 1967.

Training Program To Improve Well Control Operations

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Abstract

A well control training program has been developed to give drilling superintendents and drilling engineers the necessary understanding, skill, and practice in well control. The program was designed to 1) teach the theory of well kicks, 2) give a complete understanding of the physical equipment used for controlling kicks and 3) utilize sessions on a practice well where several gas kicks are controlled by actually implementing what has been learned in classroom seminars. The blowout prevention practice well is unique to this program and enables drilling supervisors to increase their confidence and skills under controlled conditions. During the two years that the program has been in operation, all of the drilling personnel in South Texas and many from other company operations have utilized the practice well. The handling of well kicks plus the increased confidence of the supervisors in all phases of drilling operations proves the tangible and reoccuring benefits of the training program.

Introduction

Approximately 160 wells per year are drilled in Humble's South Texas Division area. These range in depth from 4,000 to 20,000 feet. Formation pore pressures range from normal in the western part of the division area to 18.1 pounds per gallon in the eastern part of the area, and subsurface temperature gradients are among the highest in the nation. Also, the overall geology of the area is complicated.

In drilling such a wide variety of wells with these features that complicate drilling programs and with the necessity for obtaining adequate intermediate casing seats on about 30 percent of the wells, numerous well kicks can be expected. In order to successfully and safely drill these wells, it has been necessary to learn to handle these drilling problems. The program has been to train the drilling supervisors to know the theory of how to cope with a well kick and then practice and develop their skills at well control. The training program was initiated in April 1968, and consists of classroom seminars on all facets of deep, high-pressure drilling with special emphasis on well control. The unique phase of the program is that the drilling supervisors utilize a practice well to handle gas kicks until they become confident in the methods used and in their own capabilities.

What Is A Well Kick?

Figure 1 shows that a well kick is an influx of fluid from the formation into the wellbore. All rock formations penetrated by the bit are porous, that is they have void spaces to some degree. The pores in the rock depicted here contain either oil, gas, or water. These fluids are under a given pressure depending among other things, on how old the formation is, how it was formed, and how deeply it is buried. This pore presure is equal to the pressure caused by the weight of the overlying rock less the pressure born by the grain of rock itself.

Formations such as sandstone or limestone are permeable, that is the pores are connected and fluids can flow through them. When a permeable formation is penetrated by the rock bit, the pores are exposed and the pore pressure tries to push the fluids out of the pores into the wellbore. The only force normally opposing the influx of these fluids is the hydrostatic pressure, the pressure caused by the weight of the column of drilling fluid in the wellbore. When the pore pressure exceeds the hydrostatic pressure, the fluid from the formation will start feeding into the wellbore. Such an influx of fluid into the wellbore is called a kick.

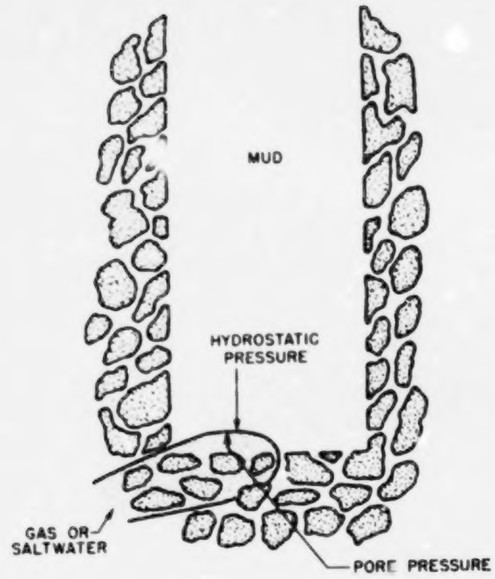
MUD
HYDROSTATIC PRESSURE
GAS OR SALTWATER
PORE PRESSURE

Figure 1. What is a kick?

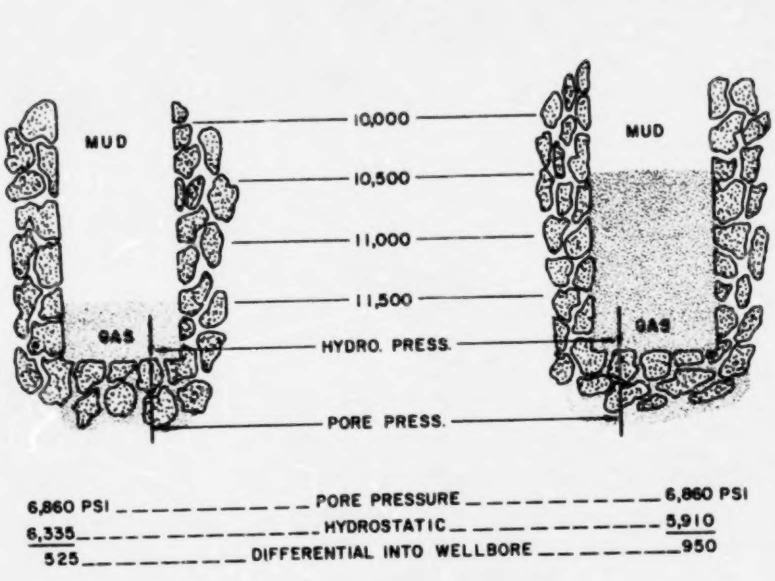
MUD
MUD
10,000
10,500
11,000
11,500
GAS
GAS
HYDRO. PRESS.
PORE PRESS.
6,860 PSI
PORE PRESSURE
6,860 PSI
6,335
HYDROSTATIC
5,910
525
DIFFERENTIAL INTO WELLBORE
950

Figure 2. What is a blowout?

What Is A Blowout?

As shown in Figure 2, a blowout is an uncontrolled influx of fluid from the formation into the wellbore. This figure shows a situation that could occur in a well. On the left side of the figure it shows that the hydrostatic pressure is 525 psi less than the pore pressure. An additional 1000 feet of gas influx into the wellbore, shown on the right side of Figure 2, decreases the hydrostatic pressure at the bottom of the hole by 425 psi so that the differential from the formation into the wellbore is 950 psi. As you can see, once the kick is experienced, it must be controlled or soon the entire wellbore will be filled with a lighter fluid. The pressures involved may develop rapidly to the point where they can no longer be controlled from the surface. Such an uncontrolled influx of fluid from the formation into the wellbore is called a blowout.

What Causes A Blowout?

Figure 3 lists the causes of blowouts. These reasons are valid for both normal and abnormal pressured formations. With insufficient mud weight, that is the hydrostatic mud pressure is less than the pore pressure, there will be an influx into the wellbore. Not keeping the hole filled means that on a trip with the drill pipe, the failure to replace the volume of the pipe withdrawn with mud will allow the fluid level to drop in the wellbore and the hydrostatic pressure to be reduced. One of the most difficult jobs on the rig today is to ascertain that the hole is taking exactly the right amount of mud while withdrawing drill pipe.

Lost circulation is the third cause of a blowout. The mud level will drop in the annulus and reduce the hydrostatic pressure below the pore pressure and influx will occur.

How Can Blowouts Be Prevented?

Blowouts can be prevented by first stopping the influx of fluids into the wellbore. The only way to stop the influx of fluids in the wellbore is to oppose the pore pressure with an equal or greater pressure. The most obvious way to stop an influx is to raise the mud weight to a hydrostatic pressure greater than the pore pressure. Sometimes this is either impractical or impossible, so we must find another way of controlling kicks. If the annular space is closed between the drill string and the casing at the surface, then no fluid will be able to leave the wellbore at that point.

1. INSUFFICIENT MUD WEIGHT
2. NOT KEEPING HOLE FILLED
3. LOST CIRCULATION

Figure 3. Causes of blowouts.

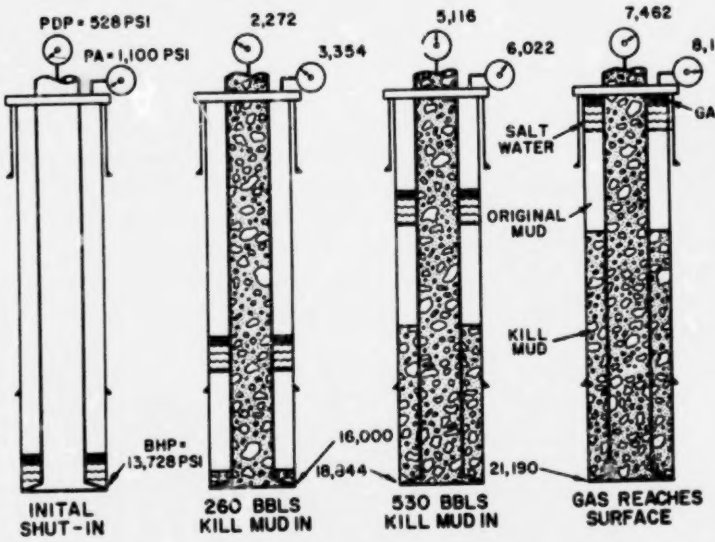
PDP = 528 PSI
PA = 1,100 PSI
2,272
3,354
5,116
6,022
7,462
8,180
SALT WATER
GAS
ORIGINAL MUD
KILL MUD
BHP = 13,728 PSI
16,000
18,344
21,190
INITAL SHUT-IN
260 BBLS KILL MUD IN
530 BBLS KILL MUD IN
GAS REACHES SURFACE

Figure 4. Excessive pressures resulting from circulation with barrels-in and barrels-out procedure.

However, formation fluids will continue to enter the wellbore until the annular pressure has built up so that the hydrostatic pressure plus the annular pressure is equal to the formation pressure.

After the influx of fluid has been stopped from entering the wellbore, then the next step is to circulate the extraneous fluid from the wellbore while preventing any further influx. In other words, the foreign fluids need to be removed from the wellbore and all surface pressures released before normal operations can be resumed. There are several methods available for controlling a kick and circulating the extraneous fluids out of the hole. The method we use is the constant drill pipe-constant bottom-hole pressure method with modifications for large kicks, casing seat pressure restriction, and surface pressures.

Results Of Mishandling A Well Kick

Figure 4 shows the magnitude of pressure that can occur when kicks are handled using the old conventional barrel in-barrel out method. Here is a well that is 16,000 feet deep; it takes a 0.6 pound per gallon kick; this means that the pore pressure is about 0.6 pounds per gallon higher at that depth than the hydrostatic pressure. The shut in drill pipe pressure is 525 psi and the well flows 70 bbl. of salt water and 5 bbl. of gas into the annulus. This influx gives 1100 psi casing pressure. By using the barrel in-barrel out method and not allowing the gas to expand as it arrives at the surface, the drill pipe pressure would become 7462 psi and the annular pressure 8180 psi. Obviously, this would break the formation down causing lost circulation, or rupture the casing. This clearly illustrates that when drilling with pressures of this magnitude, kicks must be handled correctly.

Well Control Training Program

The blowout prevention training program is an annual program and consists of the following five phases:

A seminar to discuss deep, high pressure drilling practices, This includes correct procedure for making flow checks, breaking circulation after trips and connections, use of trip tanks, pipe movement speeds, and necessary control calculations made each day for well conditions;

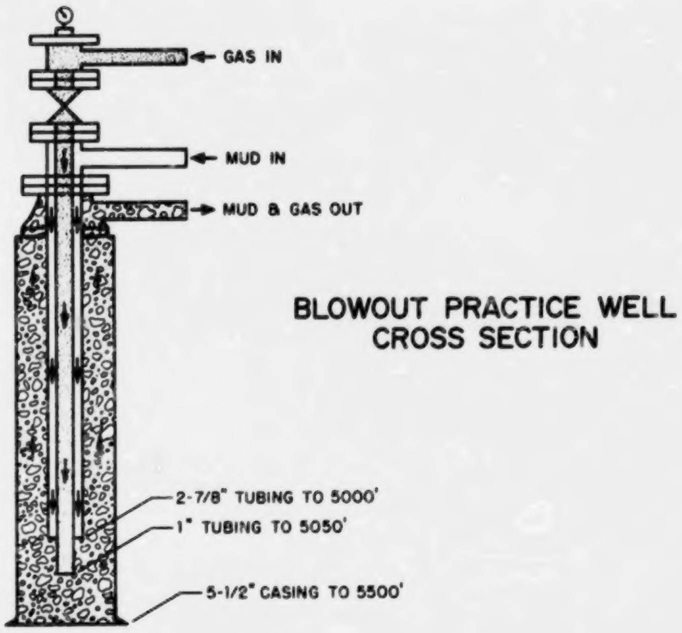

Figure 5. Blowout practice well cross section.

A seminar to study the blowout preventers and related systems, This includes a detailed study of the preventers, the hydraulic system, accumulator, hydraulic pump, source of power for the pump, Kelly cocks, Kelly safety valve, drill pipe inside blowout preventer, choke manifold, and chokes. The detailed testing procedure for each of these items of equipment is studied;

A seminar to study pore pressure determination, This seminar discusses in detail all the parameters used to determine casing seats and mud weight requirements;

A seminar to study well control, The theory of well control is investigated in detail. Modifications for wells that cannot be shut in are discussed. This session also contains the necessary mathematics to handle a well kick; and

A session at the blowout prevention practice well, Figure 5 shows the blowout prevention practice well cross

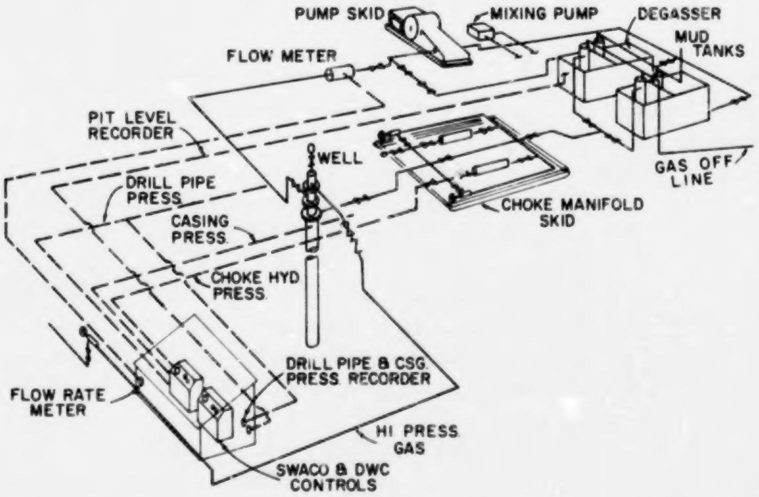

Figure 6. Blowout prevention instructional well system.

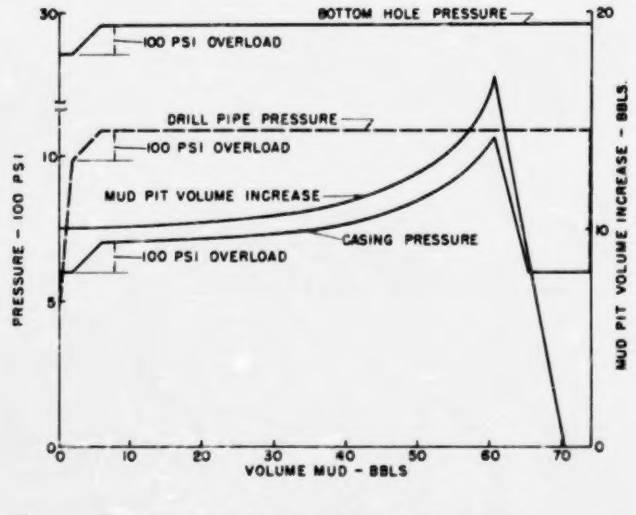

Figure 7. Constant bottom hole (drill pipe) pressure method of calculating a kick.

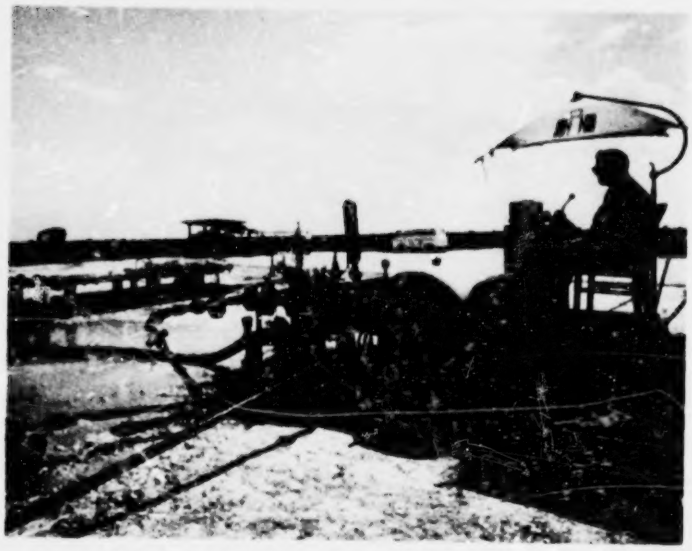

Figure 8. View of the practice well looking from the choke manifold back toward the control center. The mud pump and lines are shown in the foreground. The control center is in the background and the choke manifold is on the left.

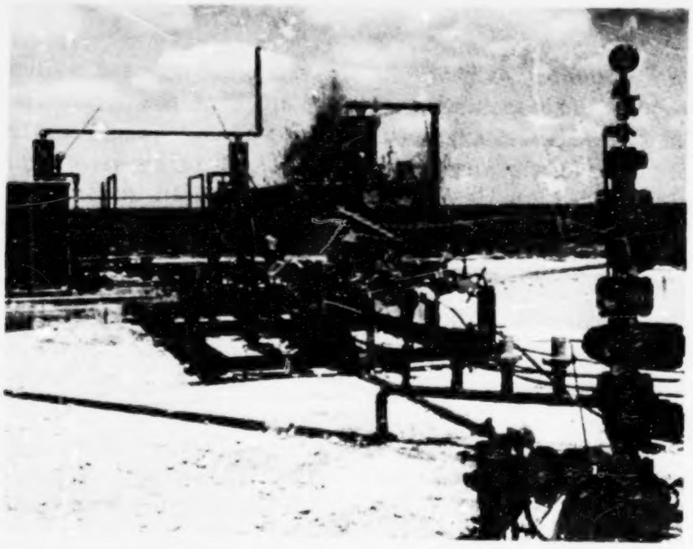

Figure 9. A view of the opposite end of the choke manifold and the mud tanks. Note the mud flying as the gas is released into the mud gas separator, well illustrating the energy contained in compressed gas.

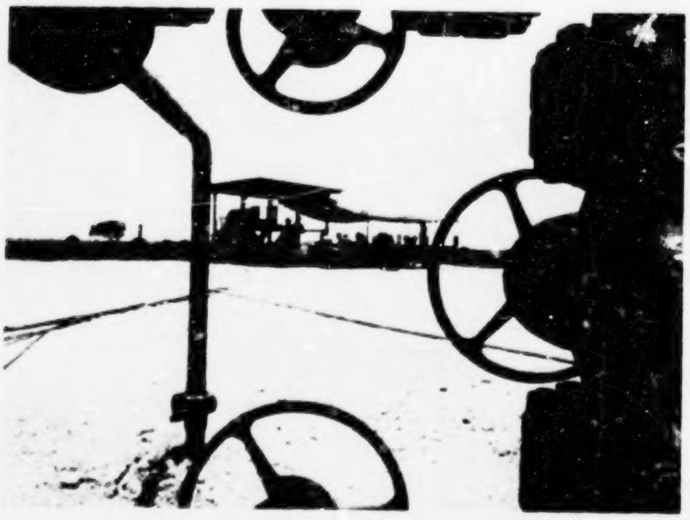

Figure 10. A view of the control center from the practice well-head.

section. It shows the well is approximately 5500 feet deep. The 5-½ inch casing, the 2-7/8 inch tubing, and 1 inch tubing are run concentrically. The annulus between the 5-½ inch and 2-7/8 inch tubing depicts the wellbore. The drill pipe is depicted by the 2-7/8 inch tubing, and high pressure gas is introduced at the bottom of the well through the 1 inch tubing. The purpose of the 1 inch tubing is only to provide for simulation of a gas kick.

Figure 6 shows a schematic of the blowout prevention practice well surface facilities. It shows the mud storage tanks on the right with the path of the mud from the tanks to the mud pump through the flow rate meter into the well down the 2-7/8 inch–1 inch annulus and back up the 2-7/8 inch–5-½ inch annulus and through the choke manifold. This choke manifold is similar to the ones normally used on the rigs, where a variable size opening can be created to partially or completely hold back pressure. From the choke manifold it goes to a mud-gas separator in the mud tanks. Mud is then picked up by the pump and pumped back into the well.

In simulating a condition that could lead to a blowout, high pressure gas is introduced through the 1 inch tubing to the bottom of the well. The control center is shown in the foreground and consists of the remotely operated choke controls, a mud flow rate meter, a gas meter run, a pit level recorder, a drill pipe pressure recorder, a casing pressure recorder, and a bottom-hole pressure recorder. The bottom-hole pressure recorder is unique to the training well. All the other items of equipment are on the drilling rigs.

Figure 7 shows a typical kick with the practice well. Gas is introduced in the bottom of the well until an 8-barrel influx is experienced. The well is shut in and has 500 psi drill pipe pressure and 600 psi casing pressure. The supervisor does the necessary calculations and decides to pump the extraneous fluid out with the same weight mud. He starts the pump and gets 100 psi overload. He then circulates the well utilizing the hydraulic chokes that are normally on the rigs.

He gets the increase in casing pressure and pit level that he expects. The bottom-hole pressure is recorded so he can see the results his actions have on bottom-hole pressure. The training well utilizes the one student-one instructor learning technique, and typically a student spends an entire day analyzing and controlling various simulated well conditions that could result in a blowout.

Conclusions

1. The type wells currently being drilled in complex geological formations often result in well kicks.
2. The objectives of the oil industry, the governmental agencies and the public are aligned in preventing blowouts. These objectives include both the prevention of economic waste and pollution.
3. The objectives of safely and economically drilling wells can best be served through the use of trained drilling personnel.
4. The five-phase training program as herein outlined has proven invaluable in Humble operations.

Oil Spill Cooperative Program

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This conference was organized to focus all of the technical, legal, political, and business talents available on the complex problems of preventing oil spills and for dealing with those spills which do occur in spite of our efforts at prevention.

I would now like to focus attention on what can be done at the local operating level to help solve these problems.

While we would like to prevent every oil spill, we know that this is not possible. Oil spills will occur, even though they can be greatly reduced by careful operations by trained personnel, so we must be prepared to deal with them and to do so promptly and effectively.

This paper deals with a principle as old as time itself–that is, help your neighbor when he's in trouble. An agreement made in advance to help a neighbor who has an oil spill is what we call an oil spill cleanup "cooperative."

For years, oil companies have had cooperative arrangements among themselves and in many locations to help one another in the event of major fires, hurricanes, and other disasters. But in 1967, the industry as a whole launched a major effort to organize cooperatives specifically to deal with oil spills.

In July of 1967, API President Frank Ikard, in formal recognition of the value of existing cooperative arrangements for handling oil spills, wrote to the chief executive officers of API member companies and called their attention to the need for forming new ones.

The primary purpose of the API effort in stimulating development of additional cooperatives was to see that, when a spill did occur at a petroleum facility, trained men and adequate equipment would be available. The petroleum industry was determined that any spills for which it was responsible would be limited as far as practical and thereby reduce any damage to public and private property and to wildlife of any kind.

The assumption at that time, as now, was that every company handling a significant volume of petroleum products should make adequate provision at each of its own installations for handling smaller spills–such as those up to 25 barrels–without outside assistance. The cooperative program was not conceived as a substitute for such preparedness on the part of individual companies.

Experience has shown, however, that oil spills cannot always be depended upon to be minor. On the contrary, accidents, equipment failures, and human frailty can be depended upon occasionally to produce spills requiring major control efforts. Advance arrangements for pooling of individual company resources to handle such spills seemed a reasonable precaution.

As might be expected, because of varying local conditions, arrangements made in developing cooperatives have not been uniform. A brief review of some of the cooperatives will show some of the variations.

With the support of the Massachusetts Petroleum Council, fourteen petroleum companies in the Boston Harbor area jointly purchased 12,500 feet of boom, motorboats, and chemicals at a total initial cost to companies of $75,000. Sections of the boom were stored at participating company installations. In the event of an emergency, the cooperative makes the boom and other

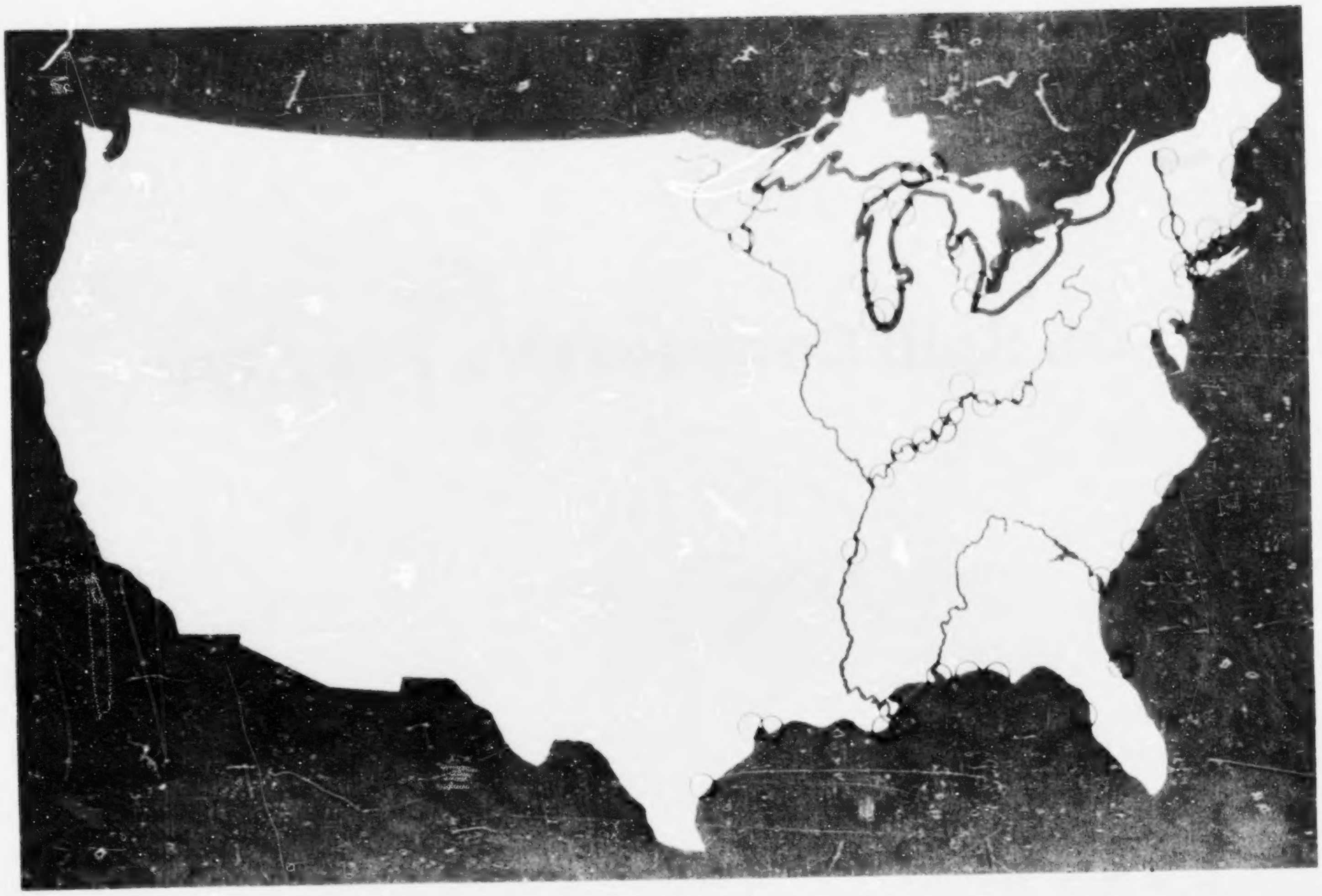

Figure 1. United States map showing location of petroleum industry oil spill clean-up cooperatives.

equipment available to the Coast Guard and other government agencies or cooperative members.

A more formal arrangement was chosen by the participating companies who formed a cooperative in Portland, Maine, area. The Portland Harbor Pollution Abatement Committee was formed and then incorporated in 1968 to foster the abatement of pollution in all forms. This includes the discharge of petroleum products and other waste material discharged into the waters of Portland Harbor and Casco Bay. The corporation seeks cooperation among the oil terminal operators and other businesses interested in the waterfronts and encourages the participation of the state and federal government representatives.

Although "cooperation" was essential for its formation, this Portland corporation might be characterized as a third-party service organization rather than a true cooperative.

A third variation was developed for the Pensacola, Florida, port area, with the help of the Florida Petroleum Council. The Pensacola Terminal Port Committee, in cooperation with the local fire department, adopted the following operation plan early in 1968:

When an accidental spill occurs at a member plant or terminal, the operations manager alerts the fire department, which in turn alerts the Coast Guard. If the spill is large, the fire department notifies the Pensacola Port Authority, which transports equipment and supplies to the scene of the accident. If additional manpower is needed, the member companies have agreed to make it available. All equipment and supplies are stored and transported by the port authority, which is reimbursed for its costs. The Florida Petroleum Council and the Pensacola Fire Department have the authority to allow non-members to use the equipment.

The Gulf of Mexico supplies us with our final example. An Offshore Operators Committee has been coordinating oil spill studies and cooperative arrangements in the Gulf for several years. This Committee has developed an impressive inventory of oil spill control equipment that is available to members along the coast from Pascagoula to Corpus Christi. On the list are boats, helicopters, and airplanes in addition to more conventional oil spill cleanup equipment and supplies. Only members of the Offshore Operators Committee are members of the cooperative but the Committee represents operators of over 99 per cent of the oil and gas production in the Gulf of Mexico.

Today, the petroleum industry has 23 cooperatives fully operational and another 27 in the development stages. A map of the United States (Figure 1) with the major waterways and harbors emphasized, shows the areas now served by cooperatives. The circles on this map indicate the location of cooperatives known to the API. Cooperatives on the West Coast are not shown, as that area has been monitored by the Western Oil and Gas Association and not by API. These cooperatives have been monitored informally and assisted by API as they developed, and their problems and opportunities have been studied by various API committees.

In July of this year the API Committee for Air and Water Conservation began a systematic examination of the entire field of cooperative cleanup programs. The examination included a major survey of all oil facilities bordering on coastal waters and navigable streams, as well as offshore facilities. The survey consisted of a six-page questionnaire distributed to API member companies to obtain information on facilities bordering on navigable waters.

The titles here (Figure 2) are those used on the questionnaire itself. Six pages were required to cover the questions exploring these titles. This data, which is still being analyzed, is enabling us to identify concentrations of oil handling facilities where a major spill might occur. When the study is complete, we will be able to determine for all major rivers, harbors, and ports, just where cooperative arrangements would be most useful and to implement plans to see that they are formed.

Data in Section II will give us information on the types and quantities of products being handled. Section III will help us identify, for each area, government facilities, manufacturing plants, power plants, and other facilities which should be considered when cooperatives are being formed. Notice that this list is not restricted to the petroleum industry. We firmly intend to encourage cooperatives to include all major users and handlers of petroleum products, so that any spill they experience can be brought under control as quickly as technology and planning will allow. Section IV will help us determine more accurately the status of existing cleanup programs. Sections V and VI will define the present availability of third-party cleanup services and equipment in each area.

More than 1,500 of these questionnaires have been returned and are now being tabulated. Hopefully, we shall very shortly be able to stimulate the development of additional cooperative arrangements on the basis of this current study.

Some of the questions that must be considered in the formation of cooperatives are as follows:

1. What kind and what quantities of equipment and supplies would be required by the cooperative, given the volume of products handled in the area?
2. Should certain specialized equipment be owned in common or should participants own all equipment as individuals?
3. Should cooperative membership include representatives of public bodies?
4. Under what conditions would cooperative members be expected to render service to other members?
5. Should the cooperative's equipment be made available to non-members or to public bodies? If so, under what conditions?
6. If the the source of a spill is unknown, should the cooperative take action and absorb the costs?
7. How should the expenses of the cooperative be pro-rated?

SECTION I IDENTIFICATION OF OIL HANDLING FACILITY

SECTION II PRODUCTS HANDLED IN FACILITY

SECTION III SURROUNDING OIL HANDLING FACILITIES

SECTION IV OIL SPILL COOPERATIVE CLEAN-UP PROGRAMS

SECTION V THIRD PARTY OIL SPILL CLEAN-UP SERVICE

SECTION VI OIL CLEAN-UP SERVICES PROVIDED AT THIS FACILITY

Figure 2. Major titles of a questionnaire used to survey cooperative oil spill clean-up programs.

These questions must be considered and answered locally, for no two situations are identical. The procedure for starting a local cooperative generally follows a pattern somewhat like this:

At the initiative of any interested participant, a meeting is called to explore the oil spill problems a local cooperative might help solve. Representatives of all major handlers, users, and suppliers of petroleum products are invited.

The chairman for such a meeting might be provided by a local port authority or a similar public agency. Certainly, all public agencies with responsibilities in this area should be invited to attend and should be kept fully informed of the progress and plans regardless of the nature of their participation. The first meeting agenda might include the questions listed above, and in addition, those pertaining to local conditions.

The group must develop contingency plans which outline clearly the steps to be taken when a major spill occurs. The model contingency plan for individual company use developed earlier this year by the API can provide useful guidelines for this portion of the organization work.

When the new group has decided upon its organizational structure, it then purchases the necessary additional equipment and supplies required, and finally, begins to train personnel. Part of this final step, which should not be overlooked, is to conduct practice runs, not only for handling and moving the equipment, but also for testing the communication and alert systems.

While some publicity may be given in the early stages of the formation of the cooperative, an effort should be made to obtain broader news coverage of the practice run in order to inform the public that a plan, and the equipment and manpower to carry it out, is in readiness to deal with all spills.

While the exact nature of the cooperative organization will vary from place to place, there are some general operating principles which, I believe, will apply in all cases.

The cooperative is based on the concept of providing mutual aid when large spills occur. In this way, all spills can be dealt with effectively without each member having to provide his own equipment for a major spill. Obviously, only those companies having equipment or those willing to purchase it can participate in such a cooperative.

Prompt action is necessary to effectively deal with a spill. Therefore, the cooperative must be designed to insure prompt action in all cases.

Participation does not relieve a member from responsibility for providing adequate equipment and supplies for dealing with a small spill (say up to 25 barrels) without the assistance of other members.

Each member must designate a point of contact at the operating level at which other members can request the loan of equipment and supplies. Authority should be delegated to the point of contact so that equipment can be made available without delay.

It should be clearly understood that it is the responsibility of the member causing the spill to bear the cost of cleaning it up.

The Coast Guard, fire department, port authority, or other such public agencies do not have to be participating members for they already have their own functions to perform when a spill occurs. However, the plan must provide for prompt notification of these agencies and for cooperation with them.

The cooperative should loan equipment and supplies to a public agency, upon request, to clean up a spill from an unknown source or a spill of a non-member. If the equipment is used for a non-member company, appropriate fees should apply. Only those costs which cannot be identified and charged to an individual member should be shared equally by all the members of the cooperative.

At some locations, it may be feasible to employ a third-party cleanup service to handle all spills for the cooperative and its members. At the present time, this is the exception rather than the rule. However, the possibility of developing such an arrangement should be borne in mind.

While it is not absolutely necessary that formal agreements be entered into, it is easy to understand why the informal cooperative arrangements are giving way to more formal ones, particularly in the larger port areas. Agreements worked out carefully beforehand, with the advice of legal counsel, have a way of being more equitable and more useful in a time of crisis.

It may be desirable for the members of a cooperative to provide trained manpower for cleanup operations. This creates a rather difficult problem of liability. Generally, under present law, a party assisting another is potentially liable for civil damages to third parties for negligent acts or omissions, including simple negligence, such as equipment failure. In today's atmosphere of "sue everybody" it is understandable that this legal problem is a stumbling block to the rapid development of cooperatives.

API has urged the inclusion of a "good Samaritan" provision in oil pollution laws, which would exempt a good Samaritan from civil damages due to simple negligence but not from those due to gross negligence. Such a provision has precedent in many state laws, where medical doctors, for example, are provided protection against civil suits arising from their efforts to help strangers, say, in an auto accident. A "good Samaritan" provision should be incorporated, preferably in federal law, since effective treatment of oil spills frequently requires crossing jurisdictional boundaries.

The petroleum industry presented a case for such a provision during the 1968 Congressional hearings, but the suggestion has not yet found support in the Congress. Hopefully, this problem of liability will be solved once its importance has been more generally recognized. On this issue, public interest does parallel private interest, I believe.

In conclusion–we in the petroleum industry are convinced of the value of the cooperatives as one of the tools for combating oil spills. The existence of a cooperative in a harbor focuses attention on the oil spill problem and thereby contributes to the prevention of spills.

The cooperatives are not by any means a panacea, but they do involve the local operating people with the problem and they can also form the base for contingency plans for whole areas. They will also result in greater cooperation between the oil industry and the state and federal authorities, which is of prime importance if we are to solve the problems quickly.

Oil Pollution Control Experience And Measures In The Delaware River Basin

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Abstract

The Delaware River Basin, in the area from Trenton, N.J., to Wilmington, Del., including the Philadelphia, Pa.–Camden, N. J. metropolitan area, is the site of one of the major municipal-industrial complexes in the United States. Enormous quantities of oil are transported, processed, and used in the area. There are continuous oil discharges in the form of wastes, as well as accidental spills, to the waters of the area.

The Delaware River Basin Commission (DRBC), in its comprehensive water resources management role, is concerned with all forms of oil pollution. The developing oil pollution control program in the Delaware River Basin includes a broad cooperative effort on the part of the Federal Government, the DRBC, the states, local agencies, and private interests. Included are preventive measures, such as special requirements in design and construction of petroleum handling and transportation facilities, and emergency planning at all levels, both public and private. An emergency alert system is operative, and a corrective action program is authorized and developing at the various levels of government and industry.

The DRBC, created in 1961 by the Congress and the legislatures of the States of Delaware, New Jersey, New York and Pennsylvania, is responsible for planning, development and control of the water resources of the 12,800 square mile Delaware River Basin (Figure 1). About seven million people live in the Basin; four million people and a heavy concentration of industry, including seven petroleum refineries and a number of oil terminals and storage facilities are clustered about the 75 mile stretch of the Delaware Estuary between Trenton, N. J. and Delaware City, Del.

Vast quantities of oil are delivered to, refined, used in, and transported across the Basin. Accidental discharges of oil have occurred frequently, polluting streams, coating shorelines, and generally interfering with water uses specified by the DRBC's Water Quality Standards. The accidents have included spills during transfer operations, sinking of vessels, rupture of pipelines, and discharges arising from human error.

DRBC Pollution Control Program

Commission activities and programs have interacted with the petroleum industry in a number of areas. The Commission's pollution control program, grounded in the Delaware River Basin Compact,[1] was formalized in its Water Quality Standards[2] which state: "Discharges shall not contain more than negligible amounts of debris, oil . . . or substances . . . that produce color, taste or odor of the water, or taint fish or shellfish flesh." Further, the Commission's Basin Regulation[3] state: "No person, firm, partnership, corporation, association or other entity . . . shall cause or permit any pollution . . . ".

Project Review. Under Section 3.8 of the Compact, "No project having a substantial effect on the water resources of the Basin shall be undertaken . . . unless it shall have been first submitted to and approved by the Commission . . . ". The DRBC has found that refinery waste treatment and petroleum handling and transfer facilities, including pipelines, adjoining or crossing streams, reservoirs, or recreation project areas are covered by this clause.

Commission review of such projects is to determine the effect, direct or potential, on the water resources. In

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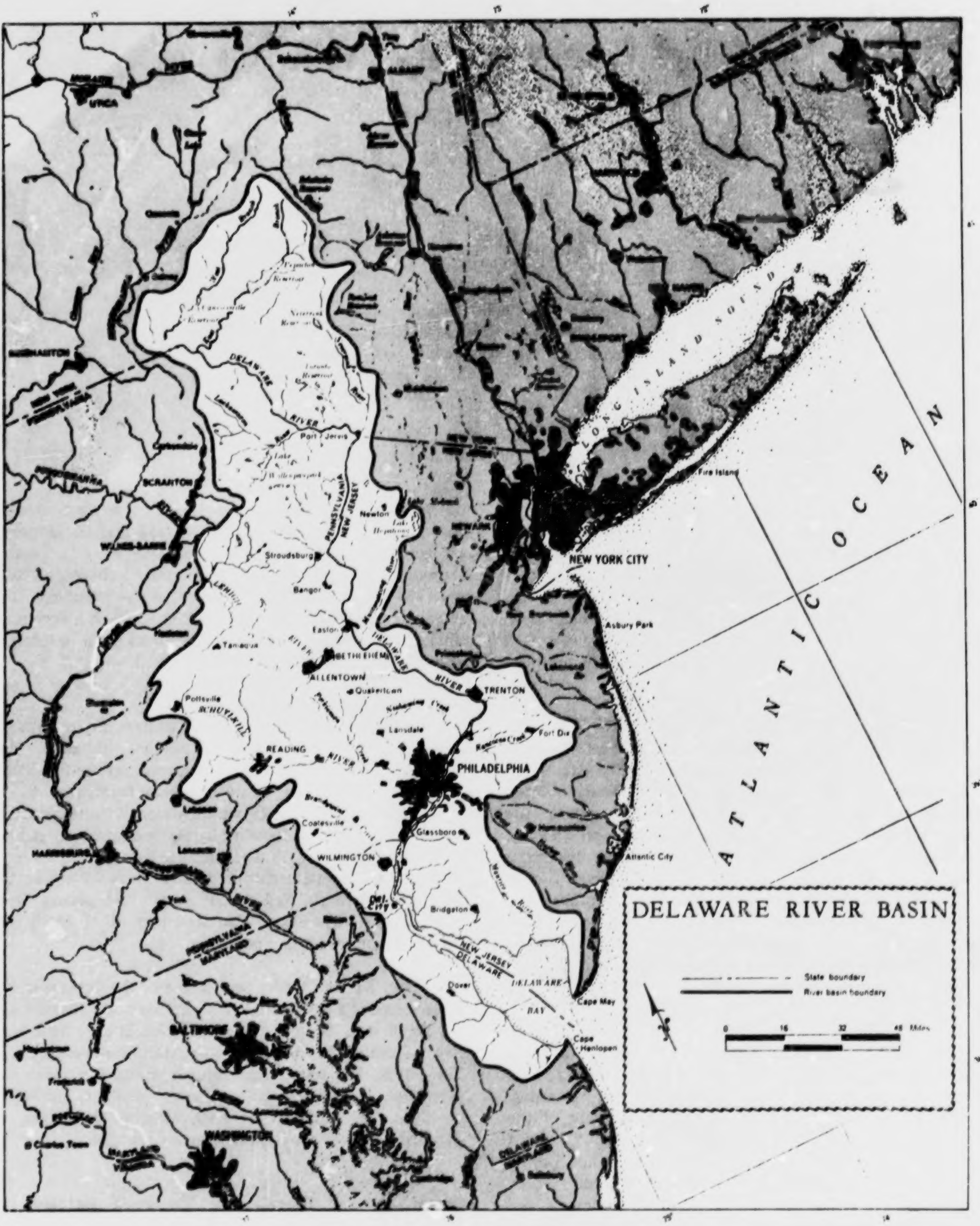
[1] Superior numbers refer to literature references at conclusion of text.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State boundary
River basin boundary
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ALLENTOWN
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WILKES-BARRE
BINGHAMTON
HARRISBURG
BALTIMORE
WASHINGTON
UTICA
NEWARK
Port Jervis
Newton
Stroudsburg
Bangor
Easton
Tamaqua
Pottsville
Quakertown
Lansdale
Fort Dix
Coatesville
Glassboro
Bridgeton
Dover
Cape May
Cape Henlopen
Atlantic City
Asbury Park
Fire Island
DELAWARE RIVER
SCHUYLKILL RIVER
LEHIGH RIVER
DELAWARE BAY
PENNSYLVANIA
NEW JERSEY
DELAWARE
NEW YORK
MARYLAND

Figure 1. Location of the Delaware River Basin.

projects involving potential pollution, special measures for the protection of the water resources may be required. There are specific limitations on all industrial waste discharges, including those from refineries. In the case of petroleum pipelines, criteria incorporating additional safety factors have been established for stream and reservoir crossings.

Other projects involving handling, transportation and processing of hazardous materials which may affect surface or ground waters are also required to be submitted for DRBC approval. Protective measures and limitations regarding the discharge of dilute forms of oil have been required as a condition of approval of industrial waste treatment facilities.

Waste Discharges. Waste treatment facilities with discharges exceeding 50,000 gallons per day and all facilities discharging toxic materials to surface or ground waters must be submitted for Commission review and approval. Such treatment facilities must comply with the Commission's Water Quality Standards, which are designed to protect the water uses specified in the Commission's Comprehensive Plan. These uses include agricultural, industrial and public water supplies, wildlife and aquatic life, recreation, navigation, and controlled and regulated waste assimilation to the extent compatible with other uses.

The seven refineries in the Delaware Estuary area have a crude capacity of approximately 38 million gallons (900,000 barrels) per calendar day. Even with careful handling of such vast quantities of oil, spill incidents occur from time to time. Of equal concern are the continuous dilute discharges of oil in various industrial wastes, resulting from the many industrial uses of oil. The numerous vessels navigating the Estuary are another potential source of oil.

Industrial Water Use. Industrial water use in the Delaware River Basin totals about 5 billion gallons per day, including 650 million gallons per day by the refineries. About 86 percent of the 5 billion gallons is used for cooling the remaining 700 million gallons per day is used in processing. If the oil content of such quantities of used water averaged only a few parts per million, a daily discharge of thousands of gallons of oil would occur.

It is likely that such quantities of oil do reach the Delaware, as attested by the numerous oil slicks visible along the river at any time.

River Sampling. Regular sampling trips are made along a 73-mile reach of the Estuary, collecting water quality samples at 17 stations. During 24 such runs between March and June 1969, oil slicks were reported at about one-third of the stations sampled (129 out of a total of 408 samples).

Recent DRB Oil Spill Experience

Between early 1960 and mid-1963, the U. S. Corps of Engineers reported 25 oil spill incidents involving pollution of the Delaware River. These spills varied from a few hundred to over 16,000 gallons. From 1963 through 1967, approximately 25 major oil and hazardous material pollution incidents, including a sunken barge accident involving over 300,000 gallons of oil, were brought to the DRBC's attention. With increased public awareness and concern over environmental pollution, 37 oil pollution incidents were reported during 1968 and 1969. These varied from heavy slicks to spills of hundreds of thousands of gallons. Identified spills resulted from tanker collision or unloading mishaps, discharges to city sewers or storm drains, and accidents at or involving refineries, oil terminals and industries. Oil barge and tank truck accidents were also involved.

The Delaware River and Estuary and a number of tributary streams were affected by these spills. Municipal and industrial water supplies were polluted, and, in some instances, shut down. Other water uses such as boating, fishing, water contact sports, and aquatic life and wildlife were severely impaired or destroyed. Smaller streams involved may take years to recover.

DRBC Activities Relating To Oil Pollution

Impaired Quality Emergency Alert and Warning System. In response to the recurring series of spills, the DRBC, in 1964, established a warning system to notify water users of impending hazards in their water supplies. The purposes of this system are threefold, as follows:

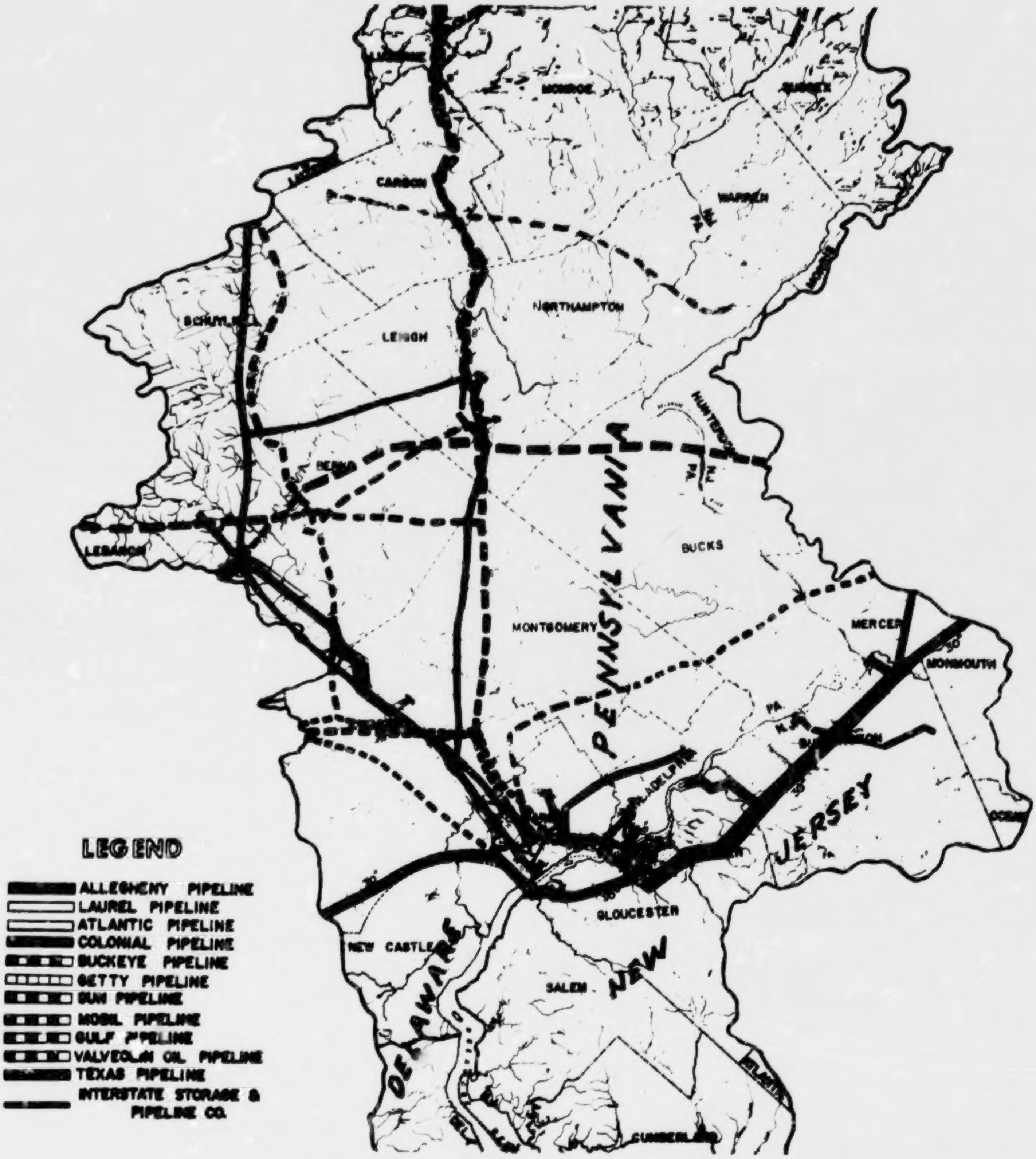
1. To protect the health and welfare of all water users.
2. To establish Basin-wide procedures for dealing with fishkill reporting and investigation.
3. To identify chronic water quality problems, including spills, unauthorized discharges, treatment plant breakdowns, etc.

This system has developed into a cooperative alert arrangement with the Basin States' water pollution control agencies. Spills have come to the Commission's attention from various sources, including government agencies, water and waste utilities, industries, and individuals. The Commission alerts appropriate Federal, state and local agencies, and coordinates state investigation and corrective actions. In extreme emergency, the Commission has alerted water users directly and participated in field investigations.

This system encompasses all forms of pollution. It has been found, however, that a high percentage of reported spills of hazardous materials involve petroleum products.

Commission Resolution No. 69-1. The National Contingency Plan[4] for combating oil and hazardous material spills, approved by the President on November 13, 1968, established a national reaction team of Federal agencies to coordinate control of massive spills, generally in excess of 10,000 gallons and affecting navigable and tidal waters. The Plan encourages the formation of state and local action teams, and the purchase of appropriate equipment and materials by states, localities and private interests.

The DRBC, on January 15, 1969, authorized emergency services to control spills. Resolution No. 69-1[5] provides for acquisition of equipment and materials and the employment of labor or the contracting with private and public entities to provide abatement services. Also authorized are agreements with state or other public agencies to provide emergency abatement services, and the recovery of costs incurred from those responsible for a spill. An expenditure account of $10,000 for each of fiscal years 1969 and 1970 was established to implement the Resolution.


MONROE
SUSSEX
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WARREN
SCHUYLKILL
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PENNSYLVANIA
MONTGOMERY
MERCER
MONMOUTH
PA.
N.J.
PHILADELPHIA
JERSEY
OCEAN
GLOUCESTER
NEW CASTLE
SALEM
NEW
DELAWARE
ATLANTIC
CUMBERLAND
LEGEND
ALLEGHENY PIPELINE
LAUREL PIPELINE
ATLANTIC PIPELINE
COLONIAL PIPELINE
BUCKEYE PIPELINE
GETTY PIPELINE
SUN PIPELINE
MOBIL PIPELINE
GULF PIPELINE
VALVEOLIN OIL PIPELINE
TEXAS PIPELINE
INTERSTATE STORAGE & PIPELINE CO.

Figure 2. Petroleum Pipelines in the Delaware River Basin.

Preventive Measures. DRBC review of projects includes consideration of preventive measures for protection of the water resources against discharges of hazardous materials. Petroleum pipelines, for example, are generally a reliable form of transportation for petroleum products. However, the vast network of possibly 200,000 miles of pipelines in the United States[6] necessarily crosses rivers, streams, watersheds and ground water recharge areas. While major failures of these pipelines resulting in water pollution have been comparatively few, it has been stated:[7] "Spills from pipelines apparently offer the greatest threat of pollution of public water supply sources." This has been the experience in the Delaware River Basin, which has almost 1100 miles of petroleum products pipelines (Figure 2). In recent years petroleum pipeline failures have been involved in a number of instances where public water treatment plants have been affected. Such incidents included a spill to the Delaware near Hutchison, N. J., in 1964, and a discharge to a tributary of Brandywine Creek in 1967. There have been other pipeline failures resulting in stream pollution.

Accordingly, special safety measures such as minimum cover, heavier pipe walls, protection against corrosion and damage, additional valves, and hydrostatic tests have been required at and near water crossings as a condition of DRBC approval of pipeline projects.

Appropriate preventive measures are also required for other facilities involving the handling of hazardous materials. In order to develop and improve such safety and preventive measures, the DRBC has instituted liaison and cooperative activities with Federal, state, local technical society and industry groups.

Current And Project Programs In The DRB

The review of projects and the requirement of special protective measures, the emergency warning system, the various preventive measures, and the coordinating and investigative programs noted are being maintained and enlarged. Specific additional measures are also being planned and implemented as follows:

Equipment and Materials. On the basis of experience of the DRBC and the respective water polluion control agencies in the Basin, equipment and materials for controlling oil spills in tributary streams are being acquired by the Commission.

Service Agreements. Negotiations are under way looking forward to having existing public agency emergency crews available on a standby basis for emergency operations under DRBC supervision.

Identification of Potential Hazards. The DRBC has comprehensive data on various types of installations, both municipal and industrial, where breakdowns or accidents could occur. For example, a survey has been made of the availability of standby power at the larger municipal waste treatment plants to determine their capability for emergency operation upon power failure. It was found that emergency capability varied from excellent to poor. Where waste streams cannot be stopped, the provision of standby or storage facilities is indicated; similarly, industrial installations (including pipelines) involving petroleum or other hazardous materials are encouraged to institute "fail-safe" operating systems which will shut down, divert, store, or otherwise prevent discharges to streams under emergency conditions.

Pipeline Mapping. Disastrous pipeline failures often result from damage to pipelines from external causes. Such accidents have occurred despite nearby pipeline markers. To sharpen general awareness of the presence of petroleum pipelines, the DRBC, on the basis of data provided by the pipeline companies, is preparing maps showing petroleum products pipelines within the Basin. It is intended to make these maps available to all public and private agencies and firms which have some relationship to designing, constructing or giving permits for such activities. It is also intended to distribute them to appropriate pollution control agencies and other organizations which may be involved in emergency activities, such as fire departments and civil defense or disaster units.

State Programs. The State of Delaware Water and Air Resources Commission has provided emergency services in cooperation with municipal forces and the DRBC. The Delaware Water and Air Resources Commission has also requested legislative authorization to establish an emergency fund for corrective action, along with authority to charge investigative and control costs to the polluter.

The Pennsylvania Sanitary Water Board has established a "Pollution Incident Prevention Program" which will modify all permits and require submission of emergency planning procedures by all permittees.

Industrial Program. The petroleum industry members along the Delaware Estuary have organized an Oil Control Coordinating Committee for cooperation in the control of river oil emergencies. A handbook has been issued listing, for each company, responsible personnel to be contacted in emergencies and available emergency equipment. Effective emergency action has been taken in a number of instances. In a recent pipeline accident, equipment and personnel furnished played a key role in containing a 170,000 gallon pipeline spill in Chester Creek, Pa., and preventing the entrance of large quantities of oil into the Delaware Estuary.

Summary

The densely populated, highly industrialized portion of the Delaware Estuary constitutes a complex problem in water resources management and pollution control. The heavy and growing concentration of oil transportation, processing and using facilities has resulted in a long-standing, oil-polluted condition. The problem of reducing this pollution despite expansion and growth is being attacked under a broad program involving Federal, interstate, state and local agencies and industries. Oil pollution can be successfully controlled only by such a comprehensive cooperative effort.

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Limited Oil Spills In Harbor Areas

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Abstract

When compared on an individual basis to major oil pollution disasters, the average Navy oil spillage incident seems insignificant. However, when the cleanup costs are tallied, these limited oil spills do not appear so small. For example, a one barrel oil spill, discharged from a destroyer berthed at the Long Beach Naval Shipyard, took nine laborers, a boat operator, a truck driver, a crane operator and a supervisor one and a half days to clean up at a cost of $1,300. On the East Coast, the Norfolk Naval Shipyard spends approximately $1,000 an incident in its oil spill cleanup operations. These spills vary between 50 and 500 gallons.

From the presented data which defines the limited oil spill, three general statements are derived:

1. *Limited oil spills are a large problem due to their numerous occurrences.*
2. *Limited oil spills require proper treatment.*
3. *Limited oil spills are expensive to treat.*

This paper investigates this last statement and by so doing discloses the actual problems which contribute to the high cost of cleaning up limited oil spills. Three factors are discussed:

1. *The physical conditions affecting an oil spill.*
    - a. *Location of the slick*
    - b. *Oil Slick Movement*
        - (1) *Spreading*
        - (2) *Weather, wind and current effects*
2. *The type of equipment employed.*
    - a. *Booms*
    - b. *Chemical Dispersants*
    - c *Physical Removal*
        - (1) *Skimmers*
        - (2) *Straws*
3. *The completeness of the removal operation.*

The limited harbor oil spill is expensive and the cost is expected to rise. At the present time, the typical oil spill costs the Navy over $1,000 to clean up. This cost will increase as control agencies rightfully require more removal and more complete removal.

Oil pollution is not completely new. As early as 1754,[1] the Caspian Sea off Baku was greatly spoiled by the leakage of bulk oil cargo carried in wooden bottom ships. Oil-laden wooden barges leaked badly into the Volga in the mid-nineteenth century. Bargement contrived to reduce leakage by loading stone ballast to increase the draft. When the level of light gravity oil was thus lowered to the waterline, the hydrostatic pressure assisted in containing the cargo.

Today the premise of retention of valuable cargo remains, but there are other imperatives. Punitive provisions of oil pollution acts, public displeasure and damage awards necessitate diligence in prevention of limited oil discharges.

When compared on an individual basis to the major oil pollution disasters, these limited oil spillage incidents seem insignificant. Indeed, the quantity of oil involved is normally less than one-tenth of one percent of the quantity discharged in the course of the Santa Barbara incident. During a Navy oil pollution study, records were obtained from the California Fish and Game Commission,[2] the Southwest Division of the Federal Water Pollution Control Administration[3] and various Navy Public Works Departments which indicate that the oil spills with which we are concerned vary in size from 10 to 2,000 gallons. Of 117 spills which occurred during a one-year period,[4] at two West Coast naval installations, more than half were less than 200 gallons and only seven were more than 1,000 gallons. From January to July 1969, 33 spills were reported in the Naval Base area, Norfolk, Virginia; of this total, 22 spills

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[1] Superior numbers refer to literature references at conclusion of text.

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were less than 100 gallons and only six were greater than 1,000 gallons. During this same period in 1968, 49 oil spills were reported with approximately the same quantity distribution. Over a 15-month period in San Diego,[5] California, 147 oil spills were reported. Fifty percent of these were in range of 20 to 100 gallons, 40 per cent were 100 to 500 gallons and 10 per cent were greater than 500 gallons. Personal communication and field investigations at other naval activities indicate that these figures are representative of the situation at the major naval bases.

Based on this data, we have assumed that the normal limited oil spill ranges from 10 to 1,000 gallons with an average quantity of 50 to 100 gallons.

Again, compared to the disaster oil spills, the area of the limited harbor oil slick is minute. The area of a given quantity of oil varies inversely with its thickness. Studies by P. C. Blokker[6] indicate that an 8-knot wind may keep a layer of oil that is trapped at the end of a harbor at a thickness of one inch. Battelle-Northwest[5] reports that harbor oil slicks may reduce from 0.04 to 0.08 inches in thickness. These figures point out that there is a great variation in the ultimate thickness, and hence, the ultimate area of a given oil spill. For our discussion, however, we will use an average variation in area from 100 square feet to 3,000 square feet.

As small as these oil spills may be, when the cleaning costs are tallied, they are by no means inconsiderable. For example, a one barrel oil spill,[7] discharged from a destroyer berthed at the Long Beach Naval Shipyard, required a contractor with a crew of nine laborers, a boat operator, a truck driver, a crane operator and a supervisor, one and a half days to clean up at a cost to the Navy of $1,300. A contract, issued FY 1969 at a West Coast naval complex for oil spill cleanup, is presently estimated at $66,000. At another base the cost for oil spill cleanup in FY 1968 was close to $75,000. On the East Coast, the situation is not much better. The Naval Base in Norfolk, Virginia, spends approximately $1,000 on each oil spill incident. This adds up to tens of thousands of dollars for oil pollution cleanup each year at this base.

Why does the Navy Department and other interested agencies, spend so many non-productive dollars on oil spills limited to such small quantities? The answer lies in the fact that, in general, harbors are mutually shared by government, private, commercial, and other maritime interests. This makes speedy and proper handling of limited oil spills imperative. In 1962[8] a spill of black oil by an aircraft carrier in San Diego harbor soiled 141 pleasure craft and fishing vessels at a commercial marina. Navy and commercial cleanup crews were dispatched shortly to clean up the spill. Nevertheless, claims paid were in excess of $10,000. This amount did not include the Navy's cost of cleaning up the spilled oil, nor did it include the costs of surveys to determine damages. Immediate retention and cleanup of spilled oil is imperative to avert claims, and minimize damage to vessels and other harbor facilities. Marine life and the quality of harbor waters are not seriously threatened by limited oil spills if the proper cleanup procedures are instigated. There is the possibility, that waterfowl, which inhabit the area, may become contaminated and perish. Consequently, concern for these priceless resources also play an important role in providing for immediate retention and cleanup of limited oil spills.

From the data presented defining the limited spill, we can deduce three general statements:

1. They exist and are a problem.
2. They require proper treatment.
3. They are expensive to remove.

It is this last statement that we intend to investigate.

Based on accumulated information, ballpark figures for limited oil spill cleanup costs have been developed. The average oil spill cleanup operation costs between $1 and $12 per gallon of oil removed. The variation is dependent upon the following factors:

1. The physical conditions affecting the oil spill.
2. The type of equipment employed.
3. The completeness of the removal operation.

By discussing these three factors, the actual problems which contribute to the high cost of cleaning up limited oil spills will be disclosed. An appreciation of these problems is necessary before undertaking any cleanup operation.

Physical Conditions Affecting The Oil Spill

Location. An inherent characteristic of the limited oil spill is that it normally occurs in confined, high-use areas. These bodies of water, as we previously noted, have many uses, ranging from water contact sports and other forms of recreation to commercial and industrial service. This fact requires that prompt action be taken to clean up spilled oil. Generally, however, this operation is not carried out under the most favorable conditions. Regardless of whether an oil slick is generated by a ship or a shore facility, it generally accumulates in a congested area. Greater than 90 per cent of all oil spill cleanup activity is carried out between nested ships, between ships and the piers or under and around pier facilities. This has a great effect on the type of equipment used and the time required to clean up the oil. Ship hulls will tend to contain an oil slick and can be successfully used to this advantage. However, most piers, being open pile constructed only increase the cleanup problems. For example, oil trapped under the 200 foot wide piers at the Naval Station in Norfolk is extremely difficult to remove. (See Figure 1.)

The proximity of recreation facilities, industrial operations, wildlife refuges, water intakes and pleasure boats dictates to a large degree the type of equipment needed and the speed with which it should be employed.

Slick Movement. The edge of an oil slick can move under the influence of two separate forces; the slick can spread under a thinning action to cover more area, and it can move as a unit under the influence of current and/or wind forces. Independent work by J. A. Fay,[9] P. C. Blokker[6] and S. A. Berrigde[10] has been done in predicting the spread of oil slicks under static sea and weather forces. However, based on experience and the normal chain of events of the average limited oil spill, theoretical estimates concerning the rate of spread have little practical significance. This is because only a small quantity of oil is involved and due to the typical discharge, either a short

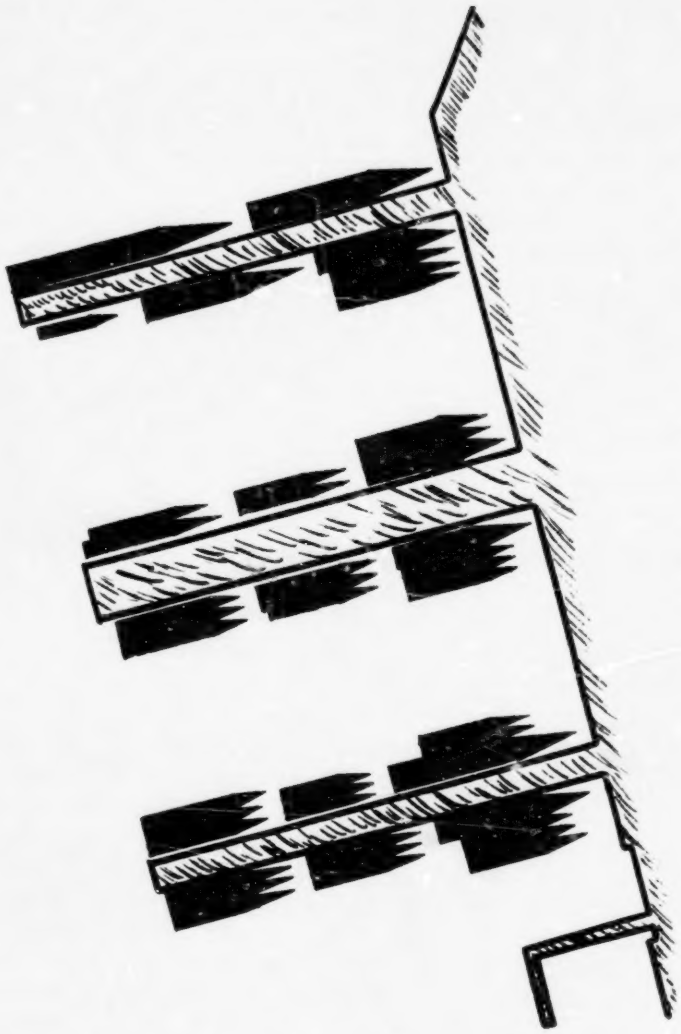

Figure 1. Typical ship berthing arrangement.

spray or a slow drip, the slick reaches its maximum area and minimum thickness very quickly.

Wind and current forces control almost the entire oil slick movement. Oil present on the water's surface, in the absense of wind and other forces, will move with the same speed as the water current. Work done by Brockis, Smith, Hughes and Polentz indicate that an oil slick[5] will move with the wind at a rate of about 3-4 per cent of the wind speed, again in the absence of additional forces. Typically, the current and wind forces will either act to force the small oil slick into a corner and hold it until it is removed, or they will solve the problem by moving the slick out to sea. When these forces act to concentrate the oil in a confined area, chemical treatment is of little use. This is due to the fact that the emulsion, formed by the action of the chemical on the oil, is not able to disperse and a mixture of 50 per cent water and 50 per cent chemical/oil is formed. This mixture is the typical "chocolate mousse" which caused so much trouble during the *Torrey Canyon* incident. Under these circumstances, physical removal is the only practical solution.

Oil spills which originate from ships moored in open bays and harbors usually find their way, again under the influence of the current and wind forces, to local pier facilities where cleanup action is initiated. However, if private boat marinas or public or commercial facilities are in danger of being contaminated, cleanup operations should be initiated in the open harbor. Generally, proper chemical dispersion is quite effective under these circumstances. However, due to the possible toxic effects of the chemical/oil mixture on the marine ecology, physical removal of the oil should be attempted first.

The combined forces of weather, wind and current significantly affect the costs of oil spill cleanup. Calm conditions will not hinder any cleanup method one might choose. Rough seas and high winds will render skimmers and other physical removal systems useless but will aid greatly in the chemical dispersion of oil slicks. Moderate sea conditions necessitate decisions by competent personnel as to equipment requirements. The methods chosen will depend upon and be effected by the experience of the operators, the physical configuration of the harbor, and the weather conditions in the slick area.

Types of Equipment Employed to Remove Oil Slicks

By thoroughly investigating the harbor conditions prior to making any purchases, the right equipment can be supplied for the job at hand, thus eliminating unnecessary and useless expenditures.

Containment. If oil booms are available, the first step in an oil spill cleanup operation should be to contain the slick, thus limiting the spread of oil and reducing the area to be cleaned. The booms used for this purpose range from homemade items, such as air-filled fire hoses, or wood and cork floats covered with rubber impregnated canvas, to proprietary equipment such as that manufactured by Neirad Industries, Sagatuck, Connecticut, or Kepner Plastics Fabricators, Inc., Torrance, California.

The general oil-boom configuration for harbor use should consist of an 8-10 foot long float, 4-8 inches in diameter with a 6-24 inch fin or skirt extending down into the water. The skirt should be weighted to keep it submerged. The booms should be supplied in lengths varying from 50-500 feet and should have the capability of being joined to form longer lengths if desired.

The use of these booms is normally limited to calm, slow-moving water, but through experience and use of the equipment, oil spills in moderately rough water can be contained. Booms can also be used to prevent oil from entering an enclosed area, such as a harbor or marina, by positioning the boom at an angle to the direction of the slick movement. A private marina in San Diego used this principal to deflect a 12,500 gallon oil slick away from its entrance. Booms should also be placed along piers or between the pier and the ship to prevent the oil from spreading or drifting under the pier.

Oil slicks can be controlled very well with high pressure water streams. By spraying the water stream on the leading edge of the slick, the oil can be contained within a restricted area such as between two ship hulls.

The proprietary oil booms range in cost from approximately $3.50 per linear foot to approximately $12 per linear foot. The cost depends on the float size, the skirt depth and the amount of ballast provided, all of which in turn depend on the general conditions of the water body in which it will be used.

Chemical Dispersants. Containing or confining an oil slick is a useless operation unless it can be chemically

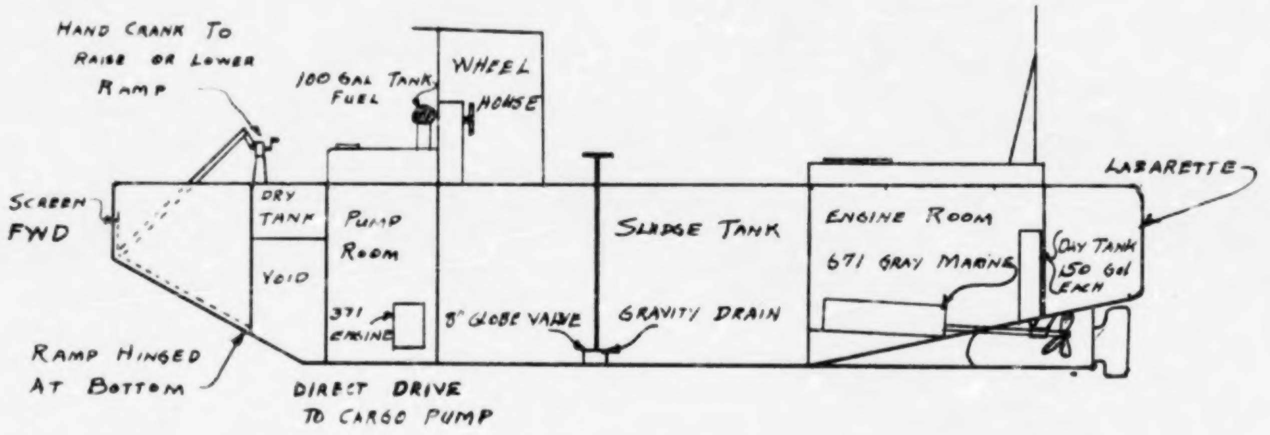
HAND CRANK TO RAISE OR LOWER RAMP
100 GAL TANK FUEL
WHEEL HOUSE
LABARETTE
SCREEN FWD
DRY TANK
VOID
PUMP ROOM
371 ENGINE
8" GLOBE VALVE
SLUDGE TANK
GRAVITY DRAIN
ENGINE ROOM
671 GRAY MARINE
DAY TANK 150 Gal EACH
RAMP HINGED AT BOTTOM
DIRECT DRIVE TO CARGO PUMP

Figure 2. Cross section showing major pieces of equipment on a converted LCM oil skimmer.

dispersed or physically removed. There are about 400 different chemicals on the market today for emulsifying and dispersing oil slicks, and their price ranges from $1.15 to $3.75 a gallon.

Generally, dispersants are composed of three parts: 1. surfactants, 2. solvents, and 3. stabilizers.[11] The surfactant reduces the surface tension between the oil and water and permits the oil to be "thinned out" or spread into a very thin layer. The function of the solvents, which comprise up to 80 per cent of the dispersant product, is to enable the surfactant, the active agent, to penetrate and mix with the oil. The solvents range from petroleum materials such as kerosene to water solvents. Petroleum based and chlorinated hydrocarbon solvents are extremely toxic to marine life in general. The third major component is composed of stabilizers which fix the emulsion once it has been formed. Following chemical application, the entire oil slick must be well agitated in order to break oil into minute microscopic particles or droplets and disperse it throughout the water. Agitation can be accomplished by spraying the oil slick with a high pressure fire hose or by using a boat wake or backwash. The emulsion thus formed is more susceptible to biological degradation due to the greatly increased surface area.

The manufacturers recommend particular methods for applying their own products but two methods are generally accepted. The dispersant can be mixed with water through an eductor, similar to those used for applying fire fighting foam, thus providing chemical application and the necessary agitation and mixing in one operation, or the chemicals can be added alone followed by the necessary agitation. The manufacturer's recommendations concerning spray and droplet size should be observed for maximum effectiveness and efficiency.

There is a time and a place for everything, and this maxim also applies to chemical dispersants. The function of the dispersant is to remove the oil from the surface and dissipate it throughout the water, where it will remain until it is biologically degraded. Keeping this fact in mind will help in evaluating individual situations where the use of chemical dispersants is being considered. It should also be

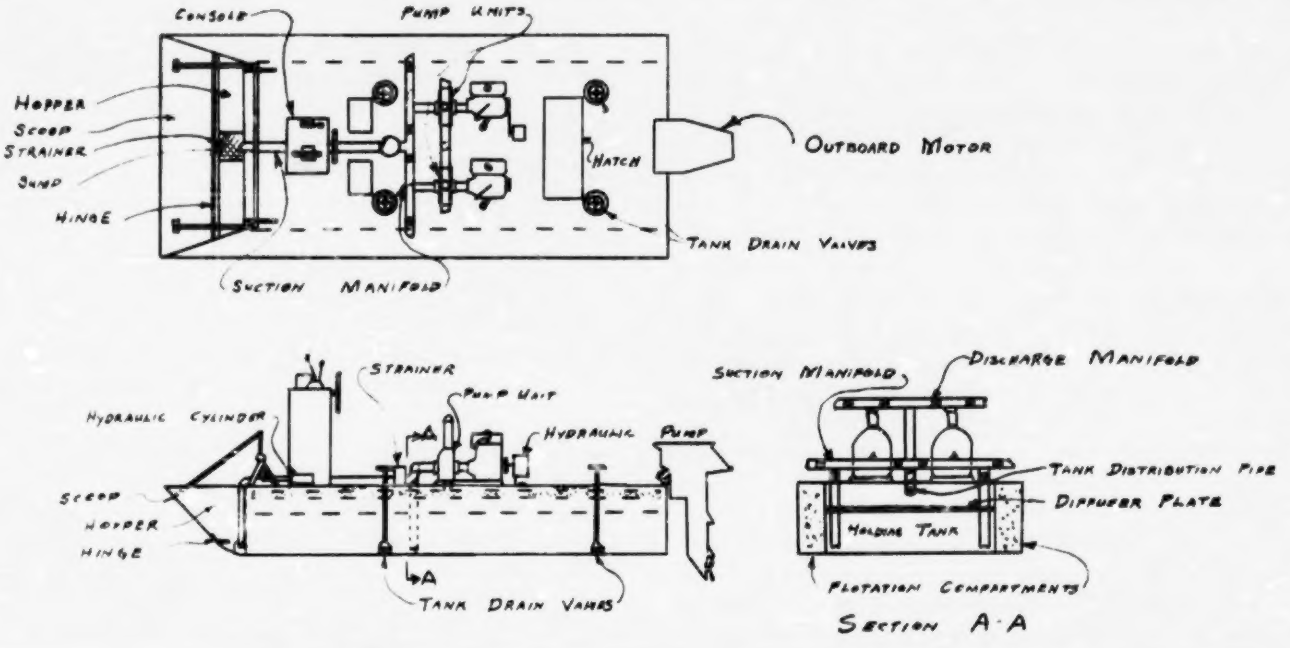
CONSOLE
PUMP UNITS
HOPPER
SCOOP
STRAINER
SUMP
HINGE
HATCH
OUTBOARD MOTOR
TANK DRAIN VALVES
SUCTION MANIFOLD
STRAINER
PUMP UNIT
HYDRAULIC CYLINDER
HYDRAULIC PUMP
SCOOP
HOPPER
HINGE
A
A
TANK DRAIN VALVES
SUCTION MANIFOLD
DISCHARGE MANIFOLD
TANK DISTRIBUTION PIPE
DIFFUSER PLATE
HOLDING TANK
FLOTATION COMPARTMENTS
SECTION A-A

Figure 3. Three views of Naval Civil Engineering Laboratory oil skimmer.

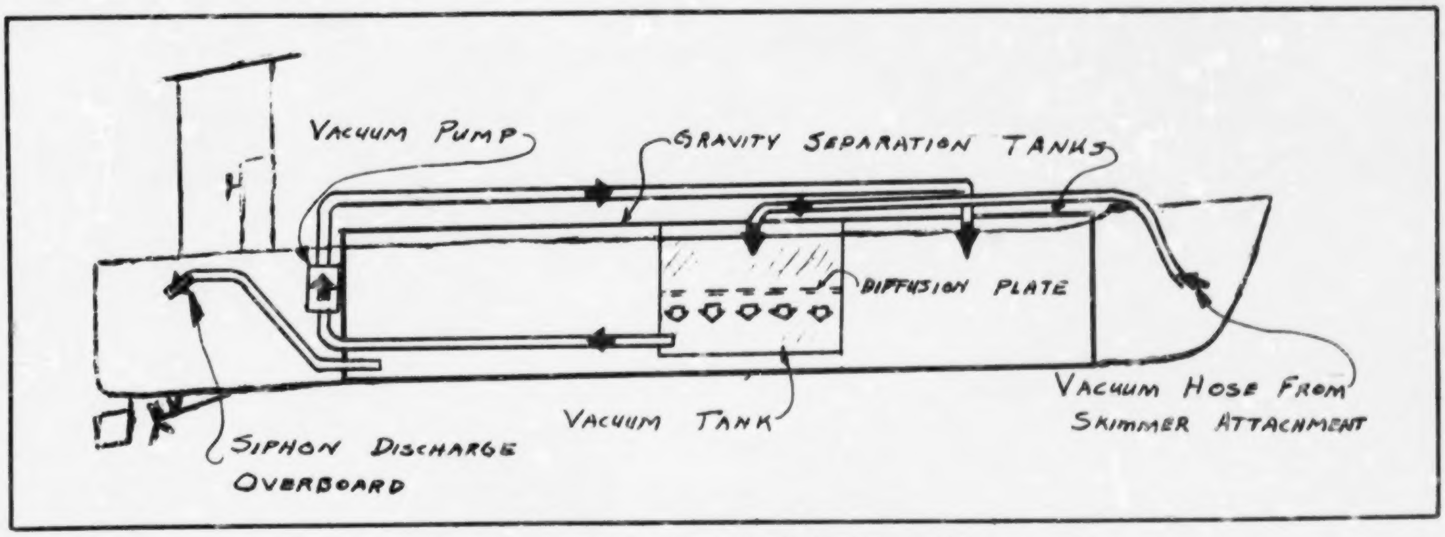
VACUUM PUMP
GRAVITY SEPARATION TANKS
DIFFUSION PLATE
VACUUM HOSE FROM SKIMMER ATTACHMENT
VACUUM TANK
SIPHON DISCHARGE OVERBOARD

Figure 4. Cross section of Veroline harbor skimmer barge.

noted that if no agitation can be provided, either naturally by wind and wave force or manually as previously mentioned, then dispersants should not be used.

Dispersants should not be used in the vicinity of shellfish beds, fish spawning areas, during fish migrations such as the seasonal salmon runs in the Northwest, near water intakes or on or near recreational beaches. Dispersants should be used to reduce a fire hazard and to protect waterfowl. They should also be used as polishing agents following the physical removal of large harbor spills and as the treating agents for small spills of up to ten gallons of oil. Due to the small quantity of oil and dispersant involved in a ten gallon spill, there is little possibility that the mixture will have a toxic effect on the marine environment. Nevertheless, the local water pollution control agency should be contacted, in any case, prior to the use of dispersants to determine if there are any restrictions on their use, and at the same time to locate the areas just mentioned that require protection. It should be noted that at no time should uncontrolled dumping of dispersants be practiced. Besides contributing greatly to water pollution, this accomplishes virtually little or no oil dispersion and wastes a large quantity of chemicals. Only controlled applications, strictly following the manufacturer's recommendations, should be permitted. As a guide, one gallon of chemical should disperse a minimum of 5 gallons of oil and the emulsion, formed by proper agitation, should last a minimum of 4 hours.

The Federal Water Pollution Control Administration is developing effectiveness and toxicity standard tests so that the numerous dispersants can be rated on a common basis. This will greatly assist the buyer in selecting the most efficient and least toxic material for his use. The Navy Department is eagerly awaiting these results.

Sinking and Burning Agents. Sinking and burning agents are mentioned only in passing because their use on the small harbor oil spill is severly limited, if permitted at all. Sinking agents, such as carbonized sand, coal dust and fly ash remove only about 50 per cent of the oil from the surface and; it is very possible that the oil will resurface again very shortly, especially if it was sunk in shallow water. This is due to agitation of the sunken oil caused by ships passing overhead or storm conditions. The use of burning agents in harbors is obviously limited because of the possibility of damaging and destroying pier structures and private and commercial ships and facilities.

Physical Removal. By far the most preferred method of oil spill cleanup, especially from the water pollution control point of view, is physical removal. To accomplish physical removal, the Navy has three different modifications of the same type of oil skimmer in operation:

1. The Norfolk Skimmer
2. The converted LCM Oil Skimmer (Figure 2)
3. The Naval Civil Engineering Laboratory Oil Skimmer (Figure 3)

All three modifications use the same basic collection method of skimming the oil over an adjustable weir into a sump and pumping the oil-water mixture from the sump into a gravity separation tank where the oil separates from the water and floats to the surface. The water is then discharged by displacement through ports or valves in the vessel's bottom. The top of the weir is usually set just below the depth of the oil on the water's surface; thus, in theory, limiting the quantity of water that can be drawn into the sump. The main problem with these units is getting the oil into the collection sump. This is accomplished by running the vessel through the oil slick or forcing the oil to the skimmer with fire hoses, oil booms or ship backwash. While these skimmers effectively separate the oil from the water, they are generally difficult to maneuver and cannot be used under piers or in close quarters due to their bulky size. The costs for these units range from about $10,000 for the NCEL Skimmer to about $30,000 for the Norfolk Skimmer.

What is really needed is a small, efficient, portable skimmer–one that can operate in close quarters, under piers, and in open water. There are several such devices that meet these requirements to varying degrees. The Navy has investigated numerous skimmers and has expressed interest in a modified Verolme Harbor Skimmer which was designed[12] by Mr. C. in 't Veld of Rotterdam and is built by the Verolme Shipyard, Heusden, The Netherlands. This skimmer (Figures 4 and 5) operates on the same principal as a household vacuum cleaner. Oil is sucked into a vacuum tank settling chamber through a floating nozzel which is connected to the vacuum tank by a long hose. Due to the fact that the oil-water mixture is not agitated and

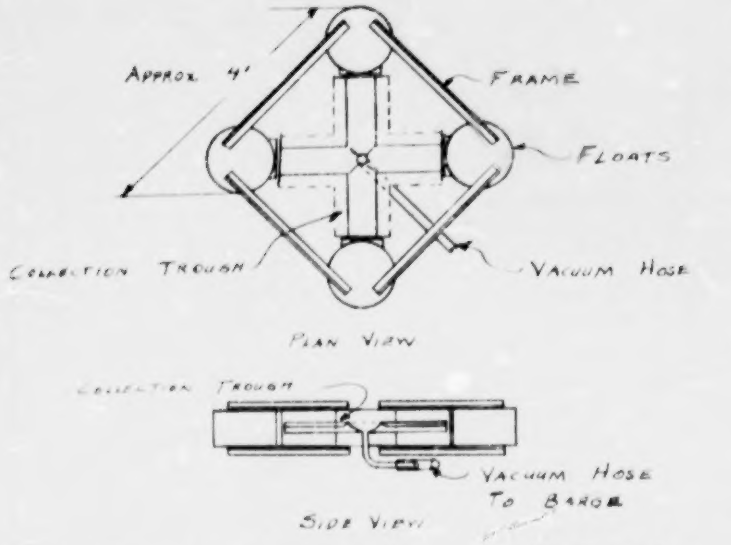

Figure 5. Two views of vacuum attachment on the Veroline harbor skimmer barge.

emulsified through a pump as it makes its way to the settling chamber, excellent oil-water separation is achieved in the tank. The vacuum is developed by pumping the water out of the tank. The nozzle permits oil to be skimmed from most areas. Being small, it floats on top of small waves and is not affected by the rising and falling of the water's surface. It is felt that a modified unit of this or a similar design would enable the Navy to achieve essentially complete physical removal of oil at its major installations.

Straw is used by a contractor at one naval base for oil slick removal. This is an expensive, messy and time-consuming operation that achieves only 65-75 per cent oil removal. The method is the same as was used at Santa Barbara; however, it is felt that its general application on the limited oil spill is not a satisfactory solution due to the incomplete removal and the generation of a harbor debris problem.

Completeness of Removal

Oil spill cleanup costs are directly proportional to the degree or completeness of removal. The amount of oil that must be removed depends on the possible effects that the remaining oil might have on the environment. These effects include property damage, destruction of marine life and damage to recreational resources. The required degree of removal will dictate the type and cost of the equipment involved. The physical parameters of the local area should, again, be thoroughly investigated in order to establish the degree of removal required prior to initiating an oil spill cleanup program. This requirement should then be discussed with the local control agencies, such as for Fish and Game and for Water Pollution Control, so that a mutual understanding can be reached. This requirement can then be used as a parameter for selecting the necessary equipment. In this way, the equipment purchased will not be "over designed" in its operations.

Conclusions

The limited harbor oil spill is expensive and the cost is expected to increase. At the present time, the typical oil spill costs the Navy $1,000 to clean up and this does not include the labor or cost of the lost product. A harbor spill involving 1,000 gallons may cost $1,700 to $4,100 to clean up.[13] This cost will rise as control agencies rightfully require more removal and more complete removal. Some states, notably California, have made the use of chemicals illegal, for any oil spill, thus limiting the choice of alternatives available.

Today's ships are tighter than the wooden barges of former times. Much oil is spilled, nevertheless, in fuel transfers, in flushing tanks, by mistakes in operating valves, by collision and groundings and by pipes, valves, lines and tanks bursting.

It is unlikely that there will be any diminution in the number of ships in operation by the Navy and other users in the foreseeable future. Further, it is apparent that the Department of Defense, Commerce, Interior, Transportation, State and Justice, in addition to port captains, fishermen, birdwatchers, claimants for reward, and irate pleasure boat owners will retain their interests in the problem.

Civil claims and suits against naval vessels have increased proportionately with the recent increase in the number of pleasure craft. Both increases will continue. Hundreds of claims for one oil spill are not now exceptional. Immediate cleanup of spilled oil and prompt investigations and surveys into the causes can save the expenditure of many thousands of non-productive dollars.

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The Submarine Pipeline And Single Buoy Mooring

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Abstract

The subject of the paper is introduced by means of a description of the submarine pipeline–single buoy mooring system. This description covers the components of the system, its purpose and its operation.

Discussion then centers on pollution prevention in the design and operation of such a system. In discussing design, each component of the total system is discussed. These are the submarine pipeline, the bottom manifold, the underbuoy hose, the buoy and the floating hose strings.

Discussion of operation of the system points out that methods of operation vary from one terminal to the next depending upon local conditions and the operator's preference. However, a generalized description is given of mooring the tanker, connecting the floating hoses, loading or off-loading cargo, disconnecting the floating hoses and leaving the mooring.

In conclusion the paper summarizes those areas of design and operation that must receive critical attention to maximize the pollution prevention aspects of the system and to insure that these systems continue to improve and continue to have a low risk of pollution associated with their use.

The rapid growth in tanker size that has taken place in the last decade is common knowledge. This growth in tanker size has brought with it the problem of how to service these very large ships at loading and receiving terminals throughout the world. The deep draft of these vessels precludes the use of most protected harbors.

A few harbors in Europe have the depth required to handle 200,000 to 300,000 dwt tankers. Numerous other harbors in Europe and other parts of the world have projects planned or underway for deepening existing harbors or building new facilities to accommodate these ships. Even so, there will still be numerous locations where dredging of this magnitude is either physically or economically not feasible. Nearly all protected harbors on the east coast of the United States fall into this latter category.

In those areas where the provision of a protected berth is not feasible an open-water berth must be used.

There are a number of types of facilities presently used to load or off-load tankers in open water. These include sea islands, spread moorings, single point mooring structures and single buoy moorings. Of these, the single buoy mooring (Figure 1) has been most frequently installed to service today's very large tankers.

The popularity of the single buoy mooring stems from the fact that it can be installed at almost any offshore location where deep water is relatively close to shore. Water depth can be selected to suit any required tanker draft. Nearly the only limitation is that the buoy must be installed a safe distance from shoal water that could constitute a danger to the tanker while mooring or unmooring.

The submarine pipeline and single buoy mooring system, shown schematically in Figure 2, consist of a submarine pipeline from the on-shore tank farm, a bottom manifold at the end of the submarine pipeline, underbuoy hose connecting the bottom manifold with the buoy, the buoy itself, and one or more strings of floating hose between the buoy and the tanker. When moored to the buoy, the tanker can rotate or weathervane to minimize the combined force of wind, wave and current.

The submarine pipeline and single buoy mooring system was first put into use in 1959. Since that time there has been a continuous increase in the number of single buoy

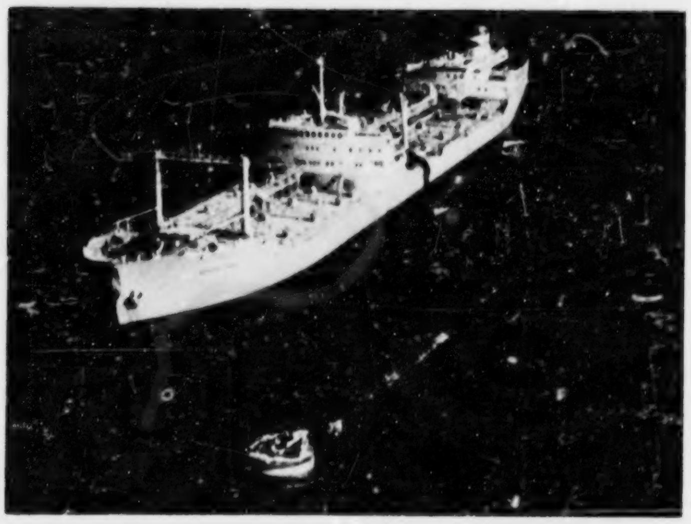

Figure 1. Tanker at the single buoy mooring.

mooring installations around the world. (Figure 3.) Recent tabulations show a total of 46 installations located in 23 different countries (Figure 4). Most of the installations put into service since 1965 have been designed for 100,000 dwt tankers or larger. Early next year a buoy designed to service 350,000 dwt tankers will be commissioned.

During the decade that the single buoy moorings have been in use there have been only a few relatively small oil spills associated with their operation. Because of the increasing popularity of the submarine pipeline and single buoy mooring system and its use for ever large tankers, it is extremely important that designs be adequate and operation be carefully controlled.

System Design

The submarine pipeline and single buoy mooring is a system. Each component, or subsystem, comprising the total system must be adequately design for the particular service that it must provide. "The chain is no stronger than its weakest link," and the prevention of oil spills depends upon every subsystem properly performing its function.

Submarine Pipeline

The submarine pipeline design must consider hydraulics, strength and durability.

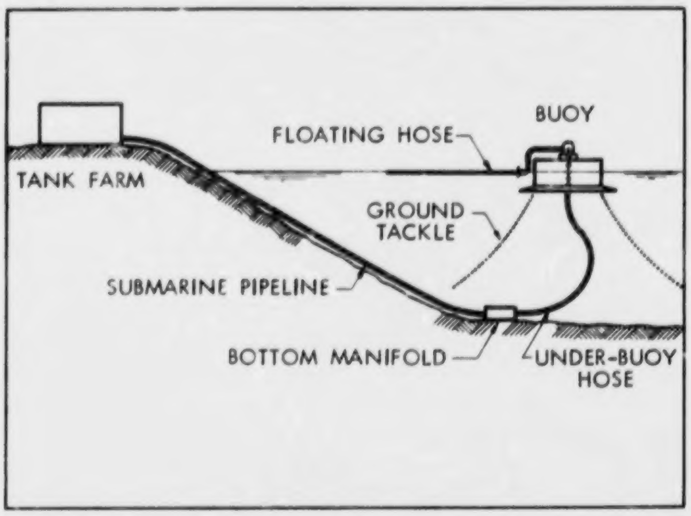

Figure 2. Schematic of the submarine pipeline – single buoy mooring system.

Hydraulics. The principle criteria for hydraulic design are the rate of flow for loading or offloading the tanker and the available head for pressure. The piping system is then designed for an acceptable pressure drop. The hydraulic design must deal with the entire system from the tank farm to the tanker. The design optimizes the sizes of the submarine pipeline, the underbuoy hose, the buoy manifold piping, and the floating hose. Pressures are generally low. For an offloading situation the pressure is usually around 100 psi but can be as high as 175 psi. In a tanker loading situation the pressure at the shore end of the submarine pipeline can be relatively high even though the pressure at the tanker manifold is generally as low as 10 to 20 psi. With the high loading and offloading rates characteristics of very large tankers, high surge pressures are possible. This problem must be eliminated by avoiding the use of quick-closing power-operated valves.

Strength. The submarine pipeline must have strength as a conduit for fluids, as a beam and as compression or tension member. It is an engineering structure subjected to a complex variety of loadings both during its construction and subsequently during its operating life. Stresses due to internal or external pressure, bending in one or more planes and axial tension or compression occur at various times and in various combinations. The force systems causing these stresses are both static and dynamic and they are applied both internally and externally. The internal forces are caused by the fluid conveyed, and the external force system includes forces caused by currents, waves, hydrostatic pressure, soil pressure, frictional forces, and restraints at anchors. Structural analysis is difficult and in some cases precise theory is lacking. Even so, it is possible to make a rational design analysis. By using the best of available technology and by taking a conservative approach where theory is weak, a safe, economical, design can be realized.

Durability. To be durable, the submarine pipeline must stay where it is constructed. It must not be subject to movement by natural forces and it must be protected against abrasion and corrosion in the marine environment. The pipeline stability problem differs depending upon whether the pipe is laid on the bottom, anchored to the bottom or buried in the bottom. Exposed pipelines are subjected to hydrostatic and hydrodynamic forces. Buried pipelines are subjected to both soil pressures and hydrostatic pressures. An exposed, anchored pipeline is subject to a combination of all of the preceding force systems.

An exposed pipeline must be designed with sufficient submerged weight that it is immovable under the action of drag, lift, and inertial forces due to currents and waves. Current forces are relatively steady and their effect on an exposed submarine pipeline are reasonably well understood. Figure 5 illustrates the force system on a submarine pipeline in an ocean current. The lift and drag produced by the current and the buoyancy must be offset by the weight and soil reactions in the system if the pipeline is to be stable on the bottom. In cases where the weight and soil reactions are insufficient, some method of anchoring can be used. The resulting force system on one type of anchored submarine pipeline is shown in Figure 6.

The action of the waves on submarine pipelines does not appear to have been sufficiently researched. Methods for determining wave forces on a pipeline resting on the

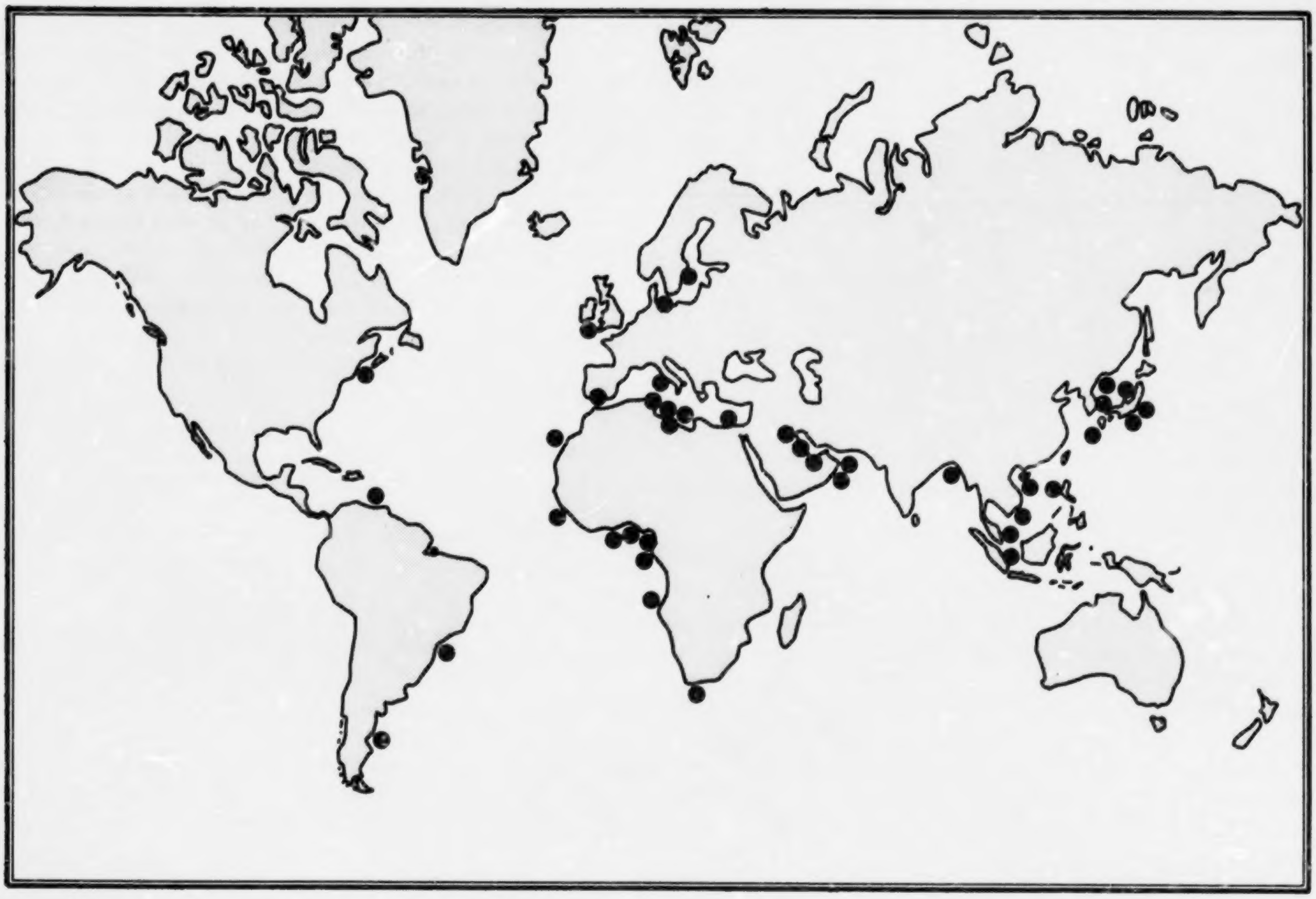

Figure 3. Geographical distribution of the submarine pipeline – single buoy mooring system.

bottom have been developed but their validity has not been tested. Figure 8 is a schematic representation of the water particle trajectories in ocean waves. The particle velocities result in lift and drag forces while the accelerations create inertial forces. A representation of the possible sequential combinations of these forces due to a passing wave is shown in Figure 9. Buried submarine pipelines must have a submerged weight that will assure that they neither sink nor float in the event of liquifaction of the marine bottom due to either differential pressures or seismic shock waves. The forces acting on a buried submarine pipeline are shown in Figure 7. The forces must be in equilibrium for the pipeline to be stable. The length of bottom spans must be controlled so that harmonic vibrations are not set up by the hydrodynamic forces associated with waves or vortex shedding.

Submarine pipelines are generally protected against the effects of corrosion and abrasion by a coating and jacketing system. A corrosion protective coating is first applied to the bare pipe. This coating is often either a conventional pipeline coat and wrap system or somastic. Other systems such as epoxy coatings, extruded plastic coatings, and sprayed thermo plastic coatings are also used. A reinforced

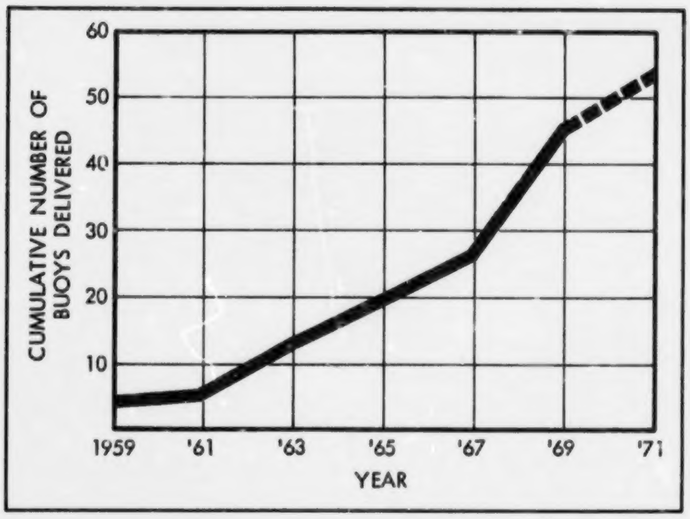

Figure 4. Growth in number of the submarine pipeline – single buoy mooring systems.

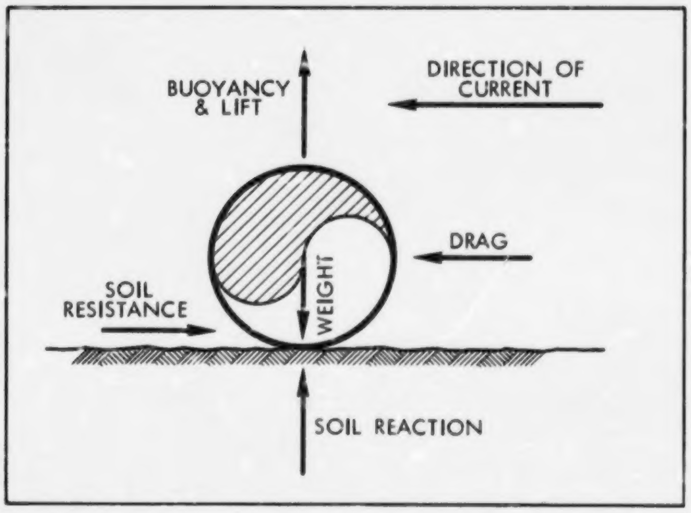

Figure 5. Force system on an exposed submarine pipeline in a current.

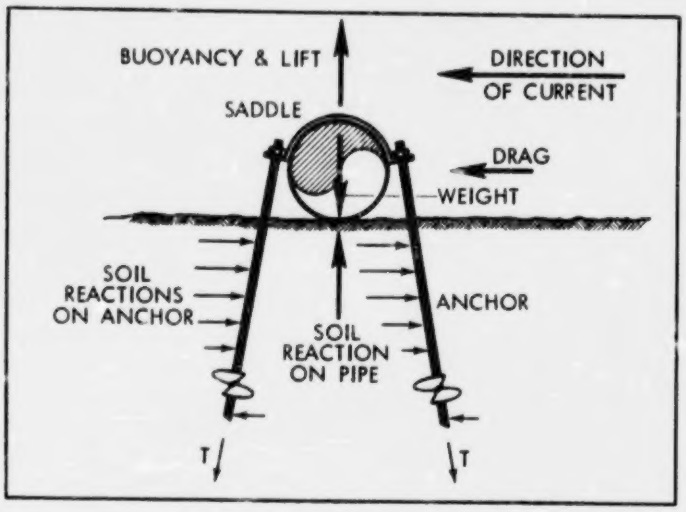

Figure 6. Force system on an exposed anchored submarine pipeline in a current.

concrete jacket is applied over the corrosion coating. This serves several purposes. It protects the corrosion coating from damage during construction, it protects the submarine pipeline from abrasion and it supplies the required submerged weight for stability of the submarine pipeline. In addition to coating and jacketing, submarine pipelines should be protected from corrosion by a cathodic protection system. Cathodic protection can be either an impressed current system, or a galvanic system using sacrificial annodes placed at intervals along the pipeline.

Under some circumstances, the submarine pipeline must always be buried. For example, the pipeline must always be buried when it passes through the surf or breaker zone. Experience has taught us that hydrodynamic forces in the surf zone can be extremely high. Further, there is a continuous and somewhat unpredictable movement of the marine bottom in this zone. Another situation which requires burial is one where the pipe, if exposed, would be subject to possible damage by dragging anchors, fish trawls, or other "outside" agencies. Under such conditions it may be necessary to specify a cover of up to 15 feet over the buried pipeline.

Bottom Manifold

The primary function of the bottom manifold is to provide for the connection of the underbuoy hoses to the submarine pipeline. The bottom manifold can, however, also serve several other important functions. Valves should be provided at each underbuoy hose connection to permit isolation of that hose for maintenance, replacement, or damage control. A sphere or scraper can be placed in the end of the submarine pipeline, beyond the underbuoy hose connections. This, along with a flooding valve at the end of the pipeline, will permit sea water to be used to displace oil for maintenance or repair. Provision should be made for anchoring the bottom manifold. Movement of this manifold could be detrimental to both the submarine pipeline and the underbuoy hoses. Figure 10 is a photograph of a bottom manifold used with a 42 inch diameter submarine pipeline.

Underbuoy Hose

The underbuoy hose strings are made up of 25 to 35 foot lengths of smooth bore, heavy duty, reinforced cargo hose flanged together. Hoses up to 24-inch diameter are currently in use and 30-inch diameter hose is said to be available.

The two methods commonly used for installing the underbuoy hose are based on the lazy "S" and the bow-legged configurations. These are illustrated in Figure 11. The lazy "S" configuration uses a steel buoyancy tank or tanks flanged into the hose string to obtain the desired curve. The bow-legged configuration is usually obtained by the use of external foam plastic flotation collars.

In either configuration the length of hose must be selected so as to avoid chafe either on the bottom, the anchor chains or the buoy, and at the same time accommodate anticipated movements of the buoy. The length is usually established either by graphics or by the use of a three-dimensional model, taking into account the tidal range and the vertical and horizontal excursion of the buoy resulting from wave action and mooring forces.

The Buoy

The buoy is made up of three basic sub-systems. These are the turntable, the hull, and the piping (see Figure 12).

Turntable. The turntable is a rotating platform on top of the buoy which serves a number of functions. It carries the mooring connections and transmits mooring line forces

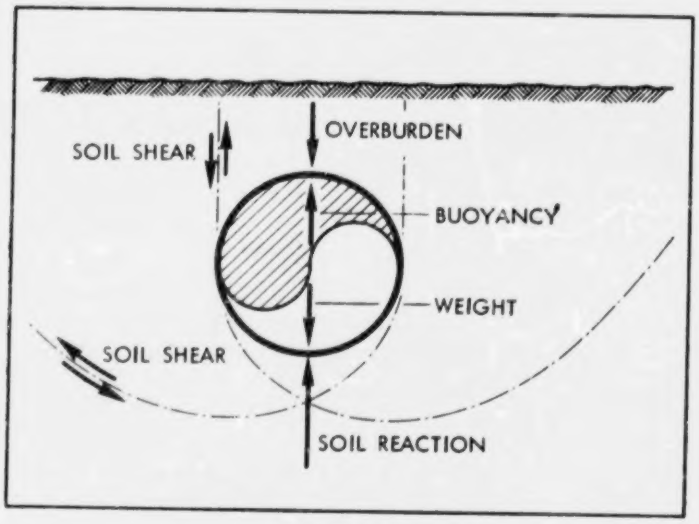

Figure 7. Force system on a buried submarine pipeline.

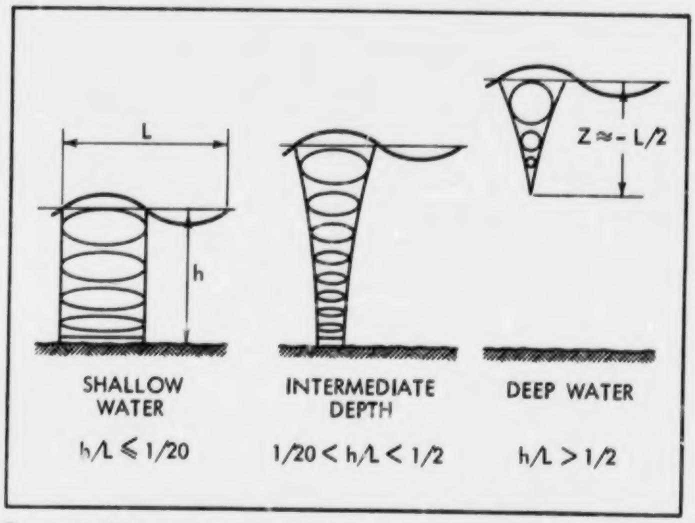

Figure 8. Schematic representation of water particle trajectories in ocean waves.

to the buoy hull through its bearings or bogey wheels. It supports the deck piping and valving. It carries a counterweight to balance the piping and the mooring fittings. It incorporates a small boat fender and access ladder, and provides a safe working platform for maintenance and repair operations. It must be designed with adequate strength and must rotate freely under all conditions of loading.

Body or Hull. The hull is the basic flotation unit required to support the ground tackle, the underbuoy hose, the buoy piping and the turntable. The hull must be designed to have sufficient reserve buoyancy that it will not be pulled underwater by the maximum anticipated mooring line forces. Further, the hull must be compartmented so that it will remain floating in the event of damage and flooding of any one compartment. The hull must be strong enough to withstand the buffeting of the sea and occasional impacts from flotsam and jetsam or small craft. It must also have sufficient strength to transmit the mooring line forces from the turntable to the ground tackle. The hull is normally designed with a skirt type fender to prevent the floating hose strings from being caught and squeezed between the ship and the buoy hull.

Piping. The piping on the buoy serves to connect the underbuoy hose through a product swivel to the floating hose.

The product swivel is the heart of the entire single buoy mooring system. It must be able to rotate through a full 360 degrees, be leak-free, and move easily. At some installations it is necessary that the swivel handle more than one product. Multi-product swivels capable of distributing up to five different products have been built.

Valves should be provided in the piping system between the swivel and each of the floating hose strings. This is to permit isolating one or more hoses for maintenance, repair, or damage control.

Mooring Lines and Ground Tackle

Both permanently attached mooring hawsers and ground tackle are part of the SBM system. Thus, mooring forces are transmitted through a known system to the ocean bottom. The maximum mooring forces are a function of a number of parameters and cannot be established analytically. Instead they are determined from analysis of the results of tests made with scale models.

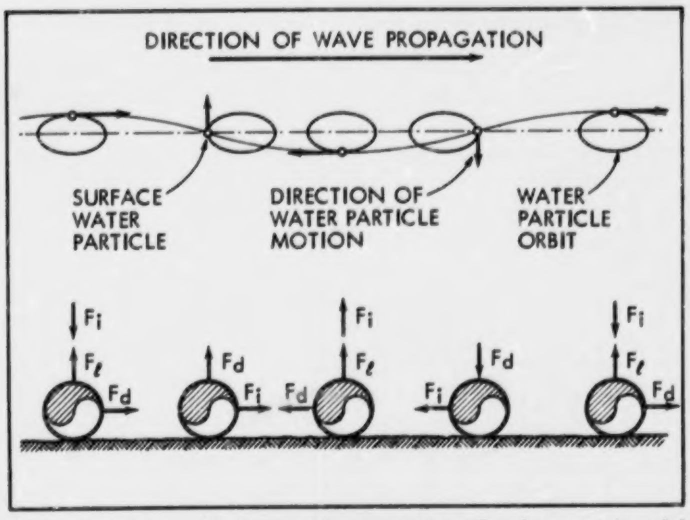

Figure 9. Schematic of possible sequential lift, drag and inertial forces exerted by a wave passing over a submarine pipeline.

Mooring Lines. Mooring lines consist of two nylon hawsers permanently connected to the buoy and made buoyant with foam plastic flotation beads. Having the mooring lines buoyant avoids the possibility of entangle-

Figure 10. Bottom manifold, 42-inch diameter submarine pipeline.

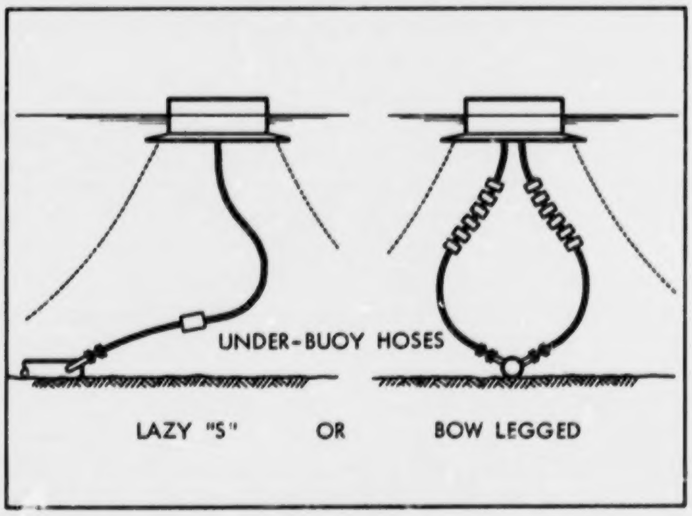

Figure 11. Two configurations for hose under a buoy.

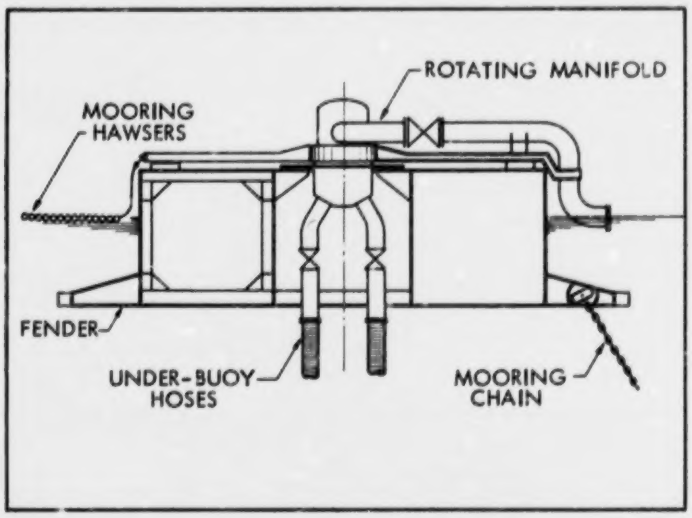

Figure 12. Buoy body and piping.

ment with the ground tackle during the periods between tankers when the buoy is not in use. Short lengths of chain are used at the ends of the hawsers where there is a danger of chafe on the buoy or on the fair leads of the ship. The high elasticity of the nylon hawsers has at least two advantages. It reduces the effective force of dynamic loadings and "snatch" caused by differential movement of the buoy and the ship. The high elasticity also leads to a better equalization of loads in the two mooring lines.

Ground Tackle. The chain and anchorage of the ground tackle array must transmit the mooring forces from the buoy to the ocean bottom. The ground tackle array forms a spread mooring for the buoy. Arrays having both four and eight legs are in common use. Other arrays are, of course, possible. Each leg of the array consists of a chain pendent from the buoy to an anchorage at the ocean bottom. A portion of the chain is constantly moving onto and off of the bottom as a result of wave action on the buoy. This "dip section" is often made of heavier chain to compensate for the extra wear that it receives. The chain pendent should be designed so that the pull on the anchorage is always parallel to the bottom even under the heaviest anticipated load condition. A small and equal pretension in each leg of the mooring reduces the excursion of the buoy when it is not in use to moor a tanker.

The type of anchorage used depends upon the soils encountered at the site. To date, both anchors and stake piles have been used as illustrated in Figure 13. Anchors, when used, should be jetted into the bottom or otherwise buried to avoid any possible dragging which would upset the balance of the system. Stake pile designs vary. The size and length of the pile depends upon the soils. The chain attachment to the pile must be designed for the repetitive dynamic loading which it must withstand.

Floating Hose Strings

The floating hose strings which form the link between the buoy and the tanker (Figure 14) are made up to 25 to 35 foot lengths flanged together. This hose is also basically a smooth bore, heavy duty, reinforced cargo hose. The length of hose that connects to the buoy is sometimes made of a special variable stiffness construction because of the severe flexing at this point. Flotation is provided either externally in the form of float collars or beads constructed of medium density unicellular plastic foam, or integrally, as a jacket of unicellular foam rubber having an external protective skin. These two systems of providing flotation are illustrated in Figure 15.

The number and diameter of the floating hoses depends upon the number of products, the desired throughput and the sizes of hose currently manufactured. Throughput for any hose is limited by velocity. The manufacturers recommend that the maximum velocity not exceed 40 feet per second. The maximum diameters available are the same as those for the underbuoy hose. Diameters of up to 24 inches are currently in use and 30-inch diameter is said to be available. For ease of operation the number of floating hoses should be kept to a minimum. Whenever possible, it is always better to use one large diameter hose in lieu of two or more of a smaller diameter.

Because of the limited capacity of tanker lifting gear and because of the stiffness of large diameter heavy duty cargo hose, 16 inch diameter hose is the largest which should be lifted over the ship's rail for connection to the manifold. Thus, when a larger diameter floating hose is used it is necessary to provide 16 inch or smaller diameter tail hoses. These tail hoses must be long enough to go from water level to the ship's manifold under all conditions of draft without excessive strain or bending which might cause kinking or other damage to the hose. The length of floating hose is a function of ship size and mooring line length. It can be determined by adding up the various elements which make up the total length between the buoy and the ship's manifold. Each tail hose should be provided with a butterfly valve and a blind flange at the end. The valve will reduce the possibility of any spill occurring when connecting or disconnecting the hose.

System Operation

From the preceding discussion of design, it should be apparent that existing technology, although lacking in some areas, is adequate for the design of a safe submarine pipeline and single buoy mooring system. However, this is only one side of the coin. The other side is operation of the system. Careful, competent operation is essential to the prevention of oil spills.

Good operating practices will vary somewhat from one terminal to the next, depending upon local conditions and

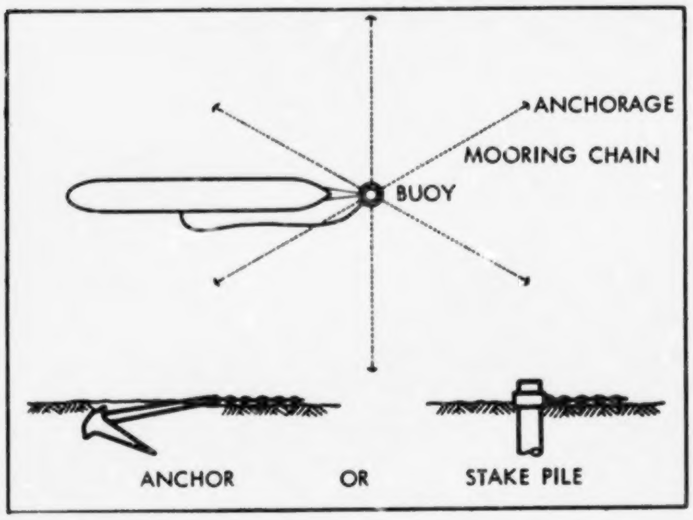

Figure 13. Ground tackle for buoy mooring.

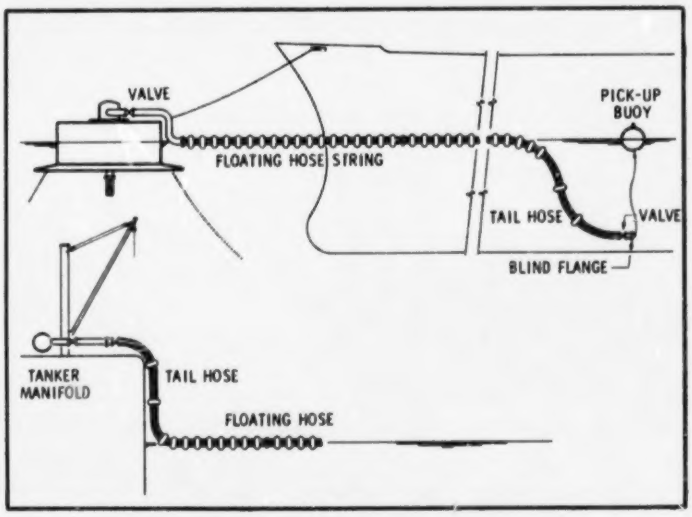

Figure 14. Floating hose string.

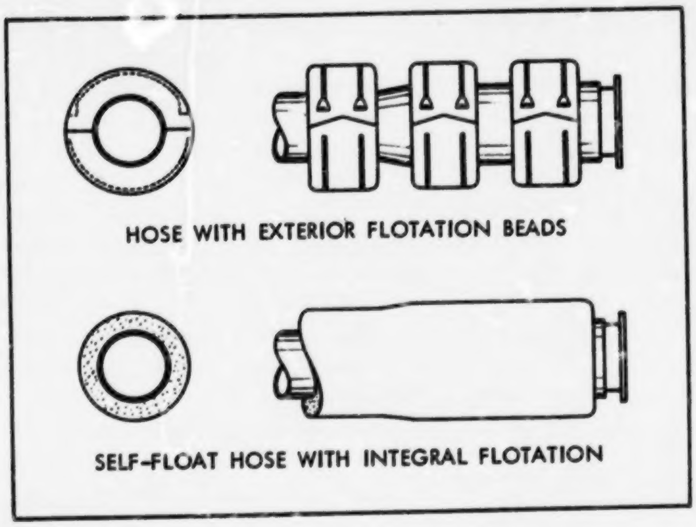
HOSE WITH EXTERIOR FLOTATION BEADS
SELF-FLOAT HOSE WITH INTEGRAL FLOTATION

Figure 15. Alternative hose flotation systems.

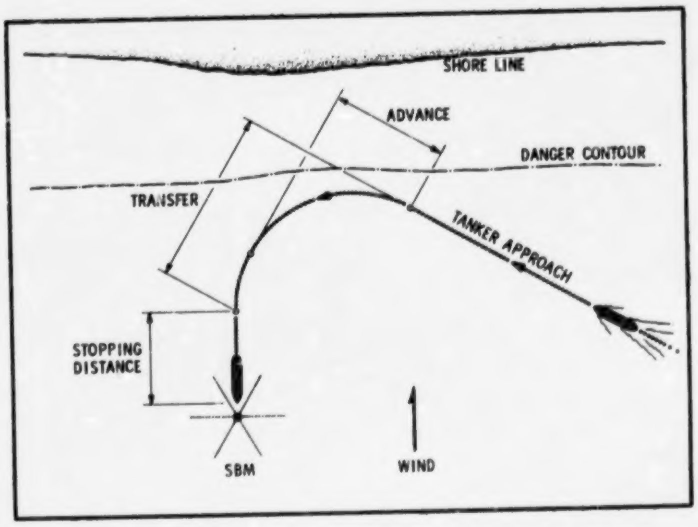

Figure 16. Diagram showing the idealized tanker approach.

the operator's preference. What follows is intended as a generalized description of the offshore operation of a submarine pipeline and single buoy mooring system.

Mooring the Tanker

Mooring of the tanker is a ship-handling problem. It is best performed under the guidance of a pilot or mooring master who is familiar with the area and the particular installation. At present, mooring of a tanker to a single buoy mooring requires the assistance of a mooring launch. This limits the mooring activity to sea conditions with wave heights of from 6 to 8 feet, or less.

Preparing to Moor. Preparation for a mooring involves the carrying out of a large number of tasks. These involve setting out the mooring gear, preparing the ship's manifolds, and planning an approach to the buoy which is consistent with the existing wind and sea conditions. If there is any chance that the tanker approach will endanger the floating hoses, the mooring launch will be advised to move the floating hose to one side.

For each installation there is a "danger contour" which represents the shoreward boundary of the safe maneuvering area around the buoy. The depth of this contour is a function of the tanker draft and the clearance required under the keel. The buoy is located so that the distance between it and the danger contour is adequate to provide for maneuvering the tanker into the berth. Figure 16 shows the danger contour and an idealized tanker approach.

The tanker will make its approach at a minimum speed consistent with ability to steer. It should complete its turn far enough from the buoy to permit adjustment in course and stopping before the buoy is reached. Ideally the ship should come dead in the water at from 100 to 300 feet from the buoy. The approach should be planned so that, if the maneuver does not proceed as expected, the ship can pass the buoy on the side opposite to the hoses and make a second approach.

Running the Lines. When the tanker is close enough to the buoy, and virtually stopped in the water, the mooring launch affixes messenger lines from the ship to each of the mooring hawser pendents. The mooring hawsers are then hauled aboard and made fast to complete the mooring.

Connecting the Floating Hoses

Hose handling is normally carried out by the ship's crew with some assistance from the mooring launch crew. Connection of the hoses is thus the responsibility of the ship's cargo officer and is carried out with advice and guidance from the mooring master.

Preparations. An important part of the preparation is establishing a communications link between the ship and the shore. Usually the mooring master is in radio communication with the on-shore operating personnel. This permits discussion of cargo handling rates, signals to be used, and emergency procedures. Other preparations include the on-board measures taken to prevent spills such as the placing of drip pans under the manifolds, plugging of the scuppers, and lashing closed all sea valves connected to the cargo piping.

Flanging Up. The floating hose is lifted with the ship's gear, stopped off, and the end lowered to the ship's manifold. The flange connection to the manifold is made using a suitable gasket to ensure against leakage.

Loading of Offloading Cargo

Pumping is not permitted to commence until the ship's cargo officer has assured himself that the valves of the cargo piping system are properly set. As a further precaution, pumping is started at a reduced rate so that connections, valving and water around the vessel can be checked.

During cargo transfer, frequent inspections are made of the mooring tackle, the mooring buoy, the floating hoses, and cargo transfer operations aboard ship. In light weather there may be a tendency for the tanker to override the buoy. This should not be permitted to happen since it could result in damage to the floating hose. Running the ship's propeller a few revolutions astern is a method sometimes used to keep the tanker in it proper position. If weather deteriorates and seas become rough it may be necessary to disconnect the floating hoses from the ship's manifold to avoid damage to them. However, it is seldom that weather and sea conditions will force a tanker to leave the mooring.

When taking on cargo, the "topping off" operation is critical from the standpoint of spill prevention. It requires experienced supervision and is usually carried out at a reduced loading rate.

Disconnecting the Floating Hoses

Disconnection normally follows completion of cargo transfer but it may also be necessary to temporarily disconnect because of adverse weather and sea conditions, or to rapidly disconnect because of an emergency resulting from unforeseen events.

If emergency quick-disconnects are provided, they should be placed between the hose end valve and the ship's manifold. Then, if an emergency dictates that the tanker depart without delay, the hose end valve can be closed to prevent serious spill.

Disconnection does not begin until all of the ship and shore valves have been closed and the ends of the hoses have been cleared of oil. Clearing can sometimes be accomplished by venting. A more positive method is to pull a slight suction on the system using a small onshore evacuation pump.

As soon as hoses are disconnected, the ends are blanked off with a blind flange. The hoses are then lowered into the water with the ship's gear and towed away from the ship by the mooring launch.

Leaving the Mooring

After the hoses have been towed out of the way, the mooring hawsers are cast off and the ship is free to depart. The departure maneuver will depend upon the site, weather conditions, and sea conditions. The maneuver must be planned so that the ship passes the buoy at a safe distance on the side away from the floating hoses.

Conclusion

The significant elements of design and operation of a submarine pipeline and single buoy mooring system have been presented with the intent of giving the reader a better understanding of the problems, advantages, and disadvantages of the system. It must be borne in mind, however, that both design and operation depend upon the site selected for the installation.

Some points which should be emphasized are:

1. Very large tankers are an economic and physical fact and the need for adequate facilities to service these very large vessels must be recognized and satisfied.
2. Sheltered deep water ports capable of handling these very large tankers are few in number.
3. Provision of sheltered facilities is not feasible for either economic or physical reasons in many parts of the world. This is particularly true in many of the areas where oil is currently produced, and at a number of crude oil processing centers in the United States, Europe and elsewhere.
4. A submarine pipeline and single buoy mooring system is a safe and economical solution to the problem of servicing very large tankers. It is the solution that has been most used to date.
5. Careful and competent design and operation are essential to the continued success of the submarine pipeline and single buoy mooring system.

Areas requiring critical attention are:

1. Design of the submarine pipeline for adequate strength and durability under the most severe anticipated environmental conditions.
2. Design of the buoy and mooring to withstand the forces imposed by the moored tanker. These forces should represent the most severe weather and sea conditions for which the tanker might be expected to remain at the mooring.
3. Continuous and careful maintenance of the entire system with particular attention to the buoy swivel, and the floating hose strings.
4. Competent supervision of all operations having to do with cargo transfer. This includes connection and disconnection of the floating hoses, operation of all cargo system valving, control of pumping rates, and other shipboard precautions.

It would not be realistic to say that accidents will not happen. Emergency procedures must be worked out, and equipment must be ready to handle accidental spills in the event that they do occur. However, experience with existing installations has demonstrated that the probability of a spill can be kept very low through proper design and operation of the submarine pipeline and single buoy mooring system.

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More Cooperation In Oil Pollution Research

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Washington, D.C.

(Monday Dinner Speaker)

It is certain that I was not asked to speak on this program because of any technical contribution that might be made on the prevention and control of oil spills. I have no qualifications in this field. I am a biologist and have sufficient interest in this serious subject to seek out the journals and to read of the work and findings of qualified scientists.

For many years, during residence on the Pacific Coast, another ornithologist and myself took advantage of every opportunity to walk the beaches of Oregon, mostly in Lincoln and Tillamook Counties, and less frequently in the more southern counties. We were studying birds and bird movements and made notes on all the birds we saw, including the dead ones found along the beaches.

There were few occasions over the 17 years we lived there when we did not find oil soaked and dead or dying birds. This amounted to only a few birds in some instances and to many thousands in others.

It was obvious that oil, even in those days, was taking a steady toll of bird life. From what we know now, it also was killing or harming other animal and plant life of the ocean environment. We had no information as to where and how this oil originated, but assumed from information given to us by Navy friends that it came from the bilges of ships plying the Oregon Coast.

It is obvious from this experience and those of many other ornithologists of my acquaintance, that spilled oil, no matter its source, is taking a constant toll of bird life, particularly among the pelagic birds. We saw more of it along the Pacific Coast because we spent more time on the beaches there. And during our studies, we also found dead fur seals and fish. Some were covered with oil, but we had no way of proving what killed them.

There is no doubt in my mind that the problem is more acute today—all the legislation, safeguards, and agreements notwithstanding—because there are more ships plying the oceans, more underwater oil exploration and recovery, and more refineries, terminals, and more of everything that accidentally or deliberately introduces oil into the aquatic environment.

Not long ago, a senior biologist at the Woods Hole Oceanographic Institution reported: "Just in the past few years we are finding we can't sail anywhere in the Atlantic—even a thousand miles from land—without finding oil."

During the course of our early studies of Oregon birdlife, we found specimens of practically every pelagic bird that is even occasionally found along that beautiful coast. If my memory serves me correctly, for example, the first record of a red-legged Kittiwake south of the Aleutian Islands was an oil-soaked bird picked up on the Oregon Coast. It now is a specimen at the Patuxent Wildlife Research Center of the U.S. Bureau of Sport Fisheries and Wildlife.

Not only did we find pelagic birds such as murres, puffins, auklets, gulls, cormorants, shearwaters and others that had become victims of oil spills, but also we found numerous ducks, mostly of the diving species, although I also recall picking up a few mallards and pintails.

I have seen few birds affected by oil spills on land, but I have seen some, particularly in Texas. None of the kills of birds I experienced along the Oregon Coast occurred as a result of any spectacular disaster such as have filled the headlines in recent years. But as damaging and as unfortunate as the major accidents are, I believe the industry will agree that oil slicks arising from the bilges and the ballasted fuel tanks of ocean vessels are the most serious offenders today. Oil comes, too, from wrecks and accidents, mechanical failures, and careless handling at manufacturing plants, refineries, and terminals. All in all, a Woods Hole scientist has estimated oil spills equal at least one million metric tons a year and perhaps much more.

As you well know, the *Torrey Canyon* affair and the Santa Barbara oil spill greatly heightened public concern about the handling of oil. Those two incidents gave massive and visual proof of the direct impact of oil on the environment. I believe the public will remain sensitive to the problem and the oil industry will be operating in more of a fish bowl than ever before. The industry is aware, I believe, that various aspects of the problem are attracting the attention of more and more well-qualified specialists in the environmental disciplines. We are only at the entering stages of understanding this whole problem.

Right now, there is national concern about the possible adverse effects of the development of oil on Alaska's Arctic Coast. The Department of the Interior has issued stringent stipulations regarding the construction of the proposed 800-mile pipeline from Prudhoe Bay to Valdez, but it is not asking Congress for enough money to adequately police and inspect the project to see that the stipulations are obeyed. Apparently, the State of Alaska is even less concerned about what happens on its lands involved in the oil activity. Many conservationists have visited the area and everyone of them with whom I have talked has been very critical of the way in which the tundra is being manhandled.

I know the oil companies are flying newsmen and other writers up there to give them a first-hand look. The hope, of course, is that the industry's side of the story will get into the news. My staff has been contacted by some of these newsmen and we find they use a key phrase voiced so much by our friends in the oil industry. The tundra is a wasteland, they argue, so why does it matter what happens there? That one point, I submit, is symptomatic of the larger environmental issue in which the industry finds itself involved.

The point is that engineers and bulldozer operators are not the individuals to pass judgement on whether an area is a wasteland or of little or no moment in the overall scheme of things. They are not the ones to pass final judgment on the relationship of their activities to the environment. They may understand the physical relationships, but they do not know the ecological ones. They can converse knowingly about cubic yards and pumping capacities, but they know little or nothing about hydrocarbon concentration in aquatic organisms, the insulation shield of tundra vegetation, or any other of the complex environmental matters.

You may be aware that the tundra lichen is one of the staple foods of the caribou and that the various species of berries that grow and ripen on the tundra provide much food for great populations of birds that nest there. This vegetation is slow-growing and many studies have indicated that the lichen, for example, take 40 or more years for rehabilitation once destroyed. Destruction of this fragile vegetation is equivalent to destroying a forest area further south on the continent.

Now, the oil industry can do a good job and has done a good job in a number of places that I have been shown. It can develop wells without defacing the countryside and without destroying the vegetation. It undoubtedly costs more to operate this way, but I can tell you, although I believe you already know, that industry will be paying more and more to conduct its operations within the limitations of the environment. Business leaders now state publicly that effective environmental protection—and I emphasize effective, long-term protection as opposed to public relations demonstrations—will be a paramount factor in deciding public acceptability in the future.

It is my experience that the oil industry needs to be more uniformly responsive to this point of view. The contrast between the activities on the Kenai National Moose Range and adjoining Cook Inlet, for example, shows what operators can do if it is necessary and fail to do if they think they can get away with it. And despite their conciliatory tone, official reports of the Department of the Interior and the industry do not tell the whole story. There is serious danger that both the short and long-term effects on the environment there are being over-simplified.

In Alaska, it is my hope that the Federal and state governments and the industry will achieve new break throughs in positive actions to protect the environment. It no longer is adequate to say only that the state needs the revenues that will be generated or that the country will benefit generally from the discovery and extraction of Arctic oil, if the whole activity is undertaken in such a way as to seriously impair the environment of that largely unspoiled land. Industry still has to prove that it can explore and remove the oil in such a way as to make the least inroads on the environmental factors that are involved.

In fact, this is the challenge facing the industry everywhere, not just in Alaska, but everywhere it now operates and where it may be operating in the future. Americans, as well as the residents of some other of the world's developed nations, are environment-conscious. Today, more than ever before, people are acutely aware of the massive threat to the environment from the expansion of population and all that it entails. They are calling on their governments for the kinds of laws and regulations that will safeguard the environment, or at least minimize its further deterioration, from those who make use of its resources.

There is not the least question in my mind that we are only at the early stages of this awareness in the United States. Environmental matters will be receiving more and more consideration. These new considerations are going to require new investments and the discovery and use of new techniques. The oil industry prides itself in innovation and technological advancement. It knows that something is not necessarily right because of its practice or utility in the past. It is time for the industry to embrace these environmental considerations in a more meaningful way.

Because of the extent and nature of its activities, the oil industry will feel this pressure for environmental awareness more sharply than others. More and more, as accessible oil reserves are charted and exploited, the industry is moving into the fragile and sensitive areas of the environment, on the continental shelves and in deep water, where conditions test man's technical knowledge and equipment to the fullest. There is movement, too, into remote areas, like the Arctic, where the forces of nature pose severe tests of men and their equipment. From what we know and have experienced, I believe it is safe to say that the constant threat of accident alone is adequate to keep the industry in a state of ready alert. But the things we do not understand fully, or now are beginning to grasp, add greatly to this uncertainty.

In the coastal zone, where tides can move pollutants many miles from their point of introduction, and where the vagaries of nature constantly threaten the permanence of industry's operations, there are many more questions than answers. Operating risks are easily charted and equipment and procedures designed to lessen or minimize them. These are the physical sorts of things that are within the realm of the engineers and geologists. But let's devote a few minutes to the biological or environmental problems that are not susceptible to physical approach.

As the *Torrey Canyon* and the Santa Barbara incidents illustrated–and keep in mind that I said earlier that those two unfortunate incidents are only symbolic of the vastly greater problem of the pollution of the sea by oil–*Torrey Canyon* and Santa Barbara demonstrated that man lacks positive methods of dealing with oil once an accident has occurred.

The usual approach is to try to contain or isolate the floating oil–an attack that works rarely if at all–or to remove it from the public eye by sweeping it under the ocean's surface by means of detergents or dispersants. More animal life was killed by chemicals used in the *Torrey Canyon* accident than by the oil itself. Containment failed as an attack at Santa Barbara and you all know the loss that followed when the oil floated ashore.

But let's give some thought to the total aquatic environment, that vast area under the surface of the sea, where only patient prodding will reveal what may be going on and where we currently have the sketchiest outline of what happens when the hydrocarbon molecules enter the mainstream of the sensitive acquatic community.

In the first place, the detergents and dispersants are pollutants in themselves. In the volumes in which they may be used, they add much of an alien chemical nature to the aquatic environment. And as in the case of *Torrey Canyon* where the detergents were dissolved in low-boiling aromatic hydrocarbons, which are poisonous to man and all other organisms, the results can be immediate and catastrophic.

Crude oil and its finished products consist of other hydrocarbon fractions–low-boiling, high-boiling, olefinic–, the implications of the introduction of which into the aquatic environment are not fully understood. In weak concentrations, the low-boiling hydrocarbons have been demonstrated to produce anaesthesia and narcosis. At higher concentrations, they produce cell damage and death in many lower forms of marine animals. They also appear to be injurious to other larval and young forms of marine life. Many of these organisms are at the threshold of the complex marine food chain, whereby larger and more advanced forms feed on and are dependent on the lower forms. Man, of course, is the ultimate beneficiary of the marine productivity whereby he uses sea life for food and other purposes.

The higher boiling hydrocarbons apparently occur naturally in marine life. While perhaps not directly toxic to exposed animals, they may interfere with nutrition and reception of the chemical clues that are necessary for communication between many marine animals. More research is needed to fully understand all of this.

Suffice it to say that even if the detergents or dispersants are not toxic in themselves, their use apparently accelerates the exposure of marine life to the toxic hydrocarbons. Some of the hydrocarbon fractions are suspected to have carcinogenic activity. These hydrocarbons are stable and they can be retained and concentrated in the marine food cycle as the lesser animals are consumed by those higher up the animal ladder. Some ultimately may end up in man.

These relationships are not known firmly. Only now are they beginning to be suspected. Unknown too, is the long-term impact of dispersed oil on the marine environment itself. Limited research points to abrupt and substantial changes in animal populations. Virtually nothing is known about the effect of the oil on ocean bottoms or whether it remains in partial suspension or where it moves.

My point in this brief discussion is to emphasize that sweeping the oil under the surface of the ocean is reminiscent only of the old proverb "out of eye out of mind." It does not resolve anything as far as environmental contamination is concerned.

The problem is more profound than just removing the stain from the ocean's surface. We need less enthusiastic claims by industry of miracle chemicals that neutralize or disperse oil slicks, making them harmless and non-injurious to man's interests. The problem is not as simple as some would make it. We need less of a defensive and apologetic posture, on the part of both government and industry. We need recognition of the fact that the direct and allied activities of the oil industry represent a substantial threat to the environment and that precautions are needed at every stage of the exploration, extraction, and handling of oil. We need less reaction and more cooperation in pushing for research to get the answers that are required.

The industry must insist on better cooperation from its own people and from allied operators who use and have petroleum products. The industry had better realize that an indifferent tanker captain, a red-necked bulldozer operator, or a glib public relations specialist can be its greatest liability.

I believe that the industry recognizes many of these things, and that is why I and other conservationists are here tonight. We are here out of a sincere belief that concerned people, acting in the full spirit of cooperation, can stimulate action needed to overcome a serious problem. I offer you my cooperation in doing this, and I know that the others do.

CHEMICAL AND PHYSICAL ADDITIVES

Tuesday, December 16, 9:00 a.m.

Chairman: Paul De Falco, Jr.
Director, Pacific Southwest Region
Federal Water Pollution Control Administration

Co-Chairman: R.T. Dewling
Acting Chief, Research and Development Program
Federal Water Pollution Control Administration

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General Dispersant Theory

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Abstract

Chemical dispersants have a role in the cleanup of oil spills. However, neither dispersion nor any other current technique is a panacea for this purpose. There are situations where dispersants can be used for the benefit of our natural resources; but there are also instances where they should not be used. Similarly, there are conditions under which they are effective, as well as limits where they become ineffective. These aspects of the subject, as well as the mechanism of and basis for dispersing oil slicks, will be discussed.

An understanding of the mechanism of dispersency is of prime importance in order to appreciate the behavior and variation in effectiveness of various generic types of surface active agents in promoting oil-in-water dispersions. In this regard, the presence of naturally occurring surfactants in crude oil and their properties are discussed. Even for the same chemical agent, its efficiency can vary due to the influence of many factors such as method of application, degree of mixing, type of oil, temperature of water, amount of circulation in the body of water, etc. Some chemicals can be more sensitive to a specific factor than others. Therefore, an appreciation of mechanism and the effect of environmental and application factors is necessary in order to assess the appropriate scope of application for dispersants as a tool for the handling of oil spills.

Even though the technical principles relating to the use of chemical dispersants for oil cleanup are somewhat elementary, it is a misunderstood subject. In this paper, the mechanism and principles involved in dispersing will be reviewed. The advantages and disadvantages and specific role of a dispersant will then become more apparent.

At the outset, to put this subject in the right perspective, let me emphasize that there are seldom any universal solutions in the field of engineering science. Rather, there are several alternative solutions–some being more applicable than others under specific conditions. The area of the control and handling of oil spills is no exception. There is no single method that is ideal for all situations. Thus, a chemical dispersant to treat oil spills is a solution or "tool" that can be the most applicable approach under certain conditions.

The prevention of spills is, of course, the first consideration. If there is a spill, physical containment and removal of the oil is the most complete and the recommended approach. When sea conditions prevent the recommended approach of containment and removal, then consideration should be given to the treatment of the oil slick at sea before it can cause damage to marine fowl, intertidal marine life and shore property. When properly dispersed as fine droplets, the oil will not cling to or "wet" a solid surface; rather it maintains itself as a discrete droplet. In addition, there is evidence that the large orders of magnitude increase in interfacial area due to fine droplet formation, which correspondingly increases the rate of biodegradation: whatever happens to reduce oil in the sea–mainly bacterial action–is generally enhanced. In essence, the oil is made available to a great deal larger population of bacteria and is thereby more readily reduced.

The Behavior of Spilled Oil At Sea

Crude oil spilled on the surface of the sea has a driving force to spread and film out. The rate that the oil spreads is determined by many factors, an understanding of which is beyond the scope of this paper. However, some qualitative concepts of rates will be useful to enable one to estimate, at least approximately, the volume of oil spilled, ultimate area that may be covered, etc.

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Initially, the spreading rate of oil for a large spill is based on the volume and density of the oil–in essence, sort of a static head that overcomes other factors such as interfacial tension and oil viscosity. Expressions for spreading rate have been derived by Blokker.[1] For reasons discussed below, the behavior of the oil spill is complex. Therefore, there have been extensive empirical studies that have been reported by Berridge et al.[2] Even as early as 1930, extensive tests were conducted and reported by the U.S. Navy.[3]

The rate of spreading and resultant thickness of the oil film varies with time. Depending upon the volume of the spill, after some interval, surface tension and viscosity forces become the principle determinants. The complexity of the spreading rate equation can be appreciated when it is considered that as the film spreads, the rate of evaporation of the lighter components increases because of the increase in surface area. This, in turn, results in an increase in the oil viscosity, thereby reducing the spreading rate. Thus, spreading, in essence, is self-retarding.

The ultimate film thickness and amount of spreading is predicated on a balance of surface tension forces which is represented by a Spreading Coefficient defined as:

$$S_{o/w} = \gamma_w - \gamma_{o/w} - \gamma_o \qquad (1)$$

where:

$S_{o/w}$ = Spreading coefficient for oil on water, ergs/cm^2

γ_w = Surface tension of water phase, dynes/cm or ergs/cm^2

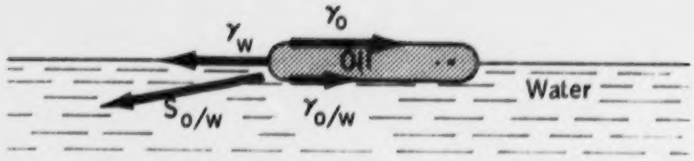
γ_o = Surface tension of oil phase, dynes/cm or ergs/cm^2

$\gamma_{o/w}$ = Interfacial tension of oil/water, dynes/cm or ergs/cm^2

This balance of surface tension forces is illustrated by Figure 1. As can be seen, if $S_{o/w}$, the resultant spreading force, is positive, the oil will spread on water; if negative, it will not spread but will remain as a "lens" of liquid. Some representative values for two different types of hydrocarbons are shown.

It is interesting to note that these two petroleum compounds are quite similar physically, i.e., same viscosity, mol weight, etc. The reason for their dissimilar spreading tendency is due to the difference in interfacial tension. More concisely, the variation in interfacial tension is due to the presence of surface active agents (surfactants) that are indigenous to the Kuwait crude oil. Surfactants that result in positive spreading coefficient for oil spreading-on-water promote dispersion of water droplets in the oil phase.

It can be seen from equation (1) why, for the same type of crude oil, a larger spreading coefficient ($S_{o/w}$) and spreading rate for oil-on-water are attained in clean sea water as opposed to a contaminated water surface. Such contamination would decrease the water surface tension, γ_w, which would, in turn, decrease $S_{o/w}$.



$S_{o/w}$, Spreading Coefficient For Oil-On-Water

$= \gamma_w - \gamma_o - \gamma_{o/w}$

For White Oil

$S_{o/w} = 72 - 33 - 52$

$= -13$

$\therefore$ White Oil Won't Spread

For Kuwait Crude

$S_{o/w} = 72 - 24 - 25$

$= +23$

$\therefore$ Kuwait Crude Will Spread

Figure 1. Spreading coefficients for oil on water.

The Properties Of The Naturally Occurring Chemical Surface Active Agents In Crude Oil

It is ironic that with the concern, in general, for purposely adding any chemical surfactants whatsoever to treat oil spills, few people realize that nature has already placed this type of compound in most crude oil. Unfortunately, the nature of these compounds promote a water droplet-in-oil emulsion rather than an oil droplet-in-water dispersion. This was evident by the water-in-oil "chocolate mousse"[4] formed after the *Torrey Canyon* and by the water-in-oil emulsions formed at Santa Barbara–both after a large amount of natural mixing energy. If nature had only provided a more hydrophilic (water compatible) surfactant in the crude, the entire aftermath might have been different.

This character of the indigenous surfactant is evident by the positive value of the spreading coefficient of oil on water for Kuwait Crude. Surface active agents that exhibit such values can be conceptually visualized to form water-in-oil emulsions by the following. As geographically illustrated in Figure 2, an oil phase that will spread on water has little ability to remain as discrete droplets in the water phase. As the oil droplet rises to the surface, it will spread as a film. A continuation of the process will result in the formation of a separate oil layer that is no longer dispersed in water. Thus directionally, the most stable dispersion of oil-in-water occurs when $S_{o/w}$, spreading coefficient for oil on water, is most negative, and $S_{w/o}$, spreading coefficient for water on oil, is most positive. The practical significance of this observation is that surface tension values are either available for most liquids or can be readily measured. Hence, spreading coefficients can be easily determined.

During a study of the behavior of these naturally occurring surfactants in crude oil, we had extracted and physically isolated this emulsifier from the crude oil.[5] The natural emulsifier, shown in Figure 3, was identified as a porphyrin compound. The behavior of the Kuwait Crude after extraction of the emulsifier was completely different in regards to spreading and forming stable water-in-oil emulsions.

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[1] Superior numbers refer to literature references at conclusion of text.

Thus, we can already appreciate the influence of surfactants on the interfacial behavior of oil and water. A petroleum compound containing no surfactants, such as the refined white oil referenced in Figure 1, or the above Kuwait Crude after extraction of its indigenous emulsifier, does not form water-in-oil emulsions. Therefore, the formation of the gelatinous "chocolate mousse" does not occur with refined products but does with most crude oils. A properly selected dispersant can prevent and/or break up this compact agglomerate of water and oil. In this regard, it is relevant to quote from a recent publication[6] of Dr. H. Hellmann of the Federal Hydrology Department, Germany, "According to all previous experience, a relatively small quantity of oil will spread out on the surface of the water, even without the addition of chemicals, and will finally reach the thickness of an oil film (about 0.1 to 0.3 microns). To be sure, without treatment this process takes substantially longer than it does after the addition of dispersing or emulsifying agents. In a strong sea or surf, spreading out of the oil is promoted on the one hand; on the other hand, the formation of a stable water-in-oil emulsion is also favored, which can float around as a compact mass on the ocean for days and can finally pollute a beach."

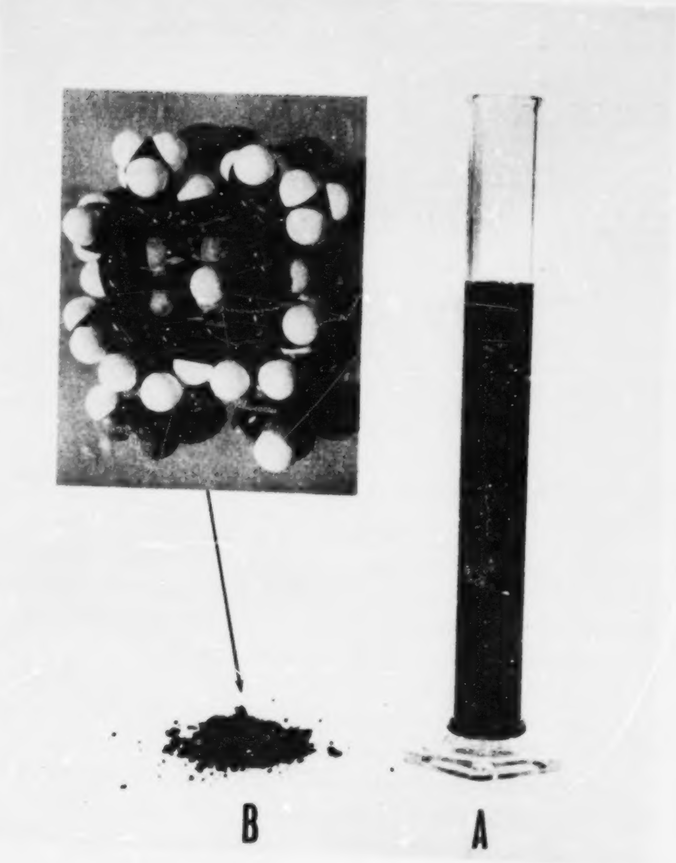

Figure 3. Natural emulsifiers extracted from Kuwait curde; A shows crude oil after extraction of emulsifiers; B is the extracted emulsifiers showing a molecular model of the key emulsifier.

The Rose And Nature Of A Surface Active Agent In Stablizing Dispersions

We have already made reference to the presence of surface active agents that occur naturally in crude oil. We define a surface active agent (surfactant) as a compound that contains both water compatible (hydrophilic) and oil compatible (lipophilic) groups. Due to this amphiphatic nature of a surfactant, it locates and arranges itself at an oil-water interface. The surfactant's molecular structure, e.g., ratio of hydrophilic to lipophilic portions, determines the type of dispersion (oil droplets dispersed in water phase or water droplets dispersed in oil phase), as well as stability of the dispersion. In essence, a surfactant that is principally water soluble disperses oil-in-water and establishes water as the continuous phase; a surfactant that is principally oil soluble, the converse. This is Bancroft's Law[7] which has been tested and proven empirically true over the years. A convenient classification for surfactants, therefore, is based on the ratio or balance of the water compatible portion to the oil compatible portion—sometimes referred to as HLB (Hydrophilic-Lipophilic Balance).[8] This relationship between the molecular structure of the surfactant and the emulsion type is shown in Figure 4. The physical concept behind Bancroft's Law can be appreciated by an inspection of Figure 4. For example, it can be visualized that for a more water compatible surfactant, the physical location of the larger hydrophilic group on the outside of the dispersed oil droplets results in a more effective "fender" to parry droplet collisions and prevent droplet coalesence. The converse, locating the larger portion of the surfactant in the dispersed rather than the continuous phase, would be geometrically awkward and unstable.[9]

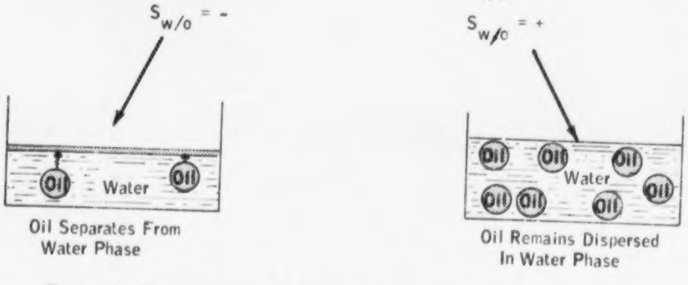
$S_{o/w}$ = Spreading Coefficient For Oil-On-Water
$S_{w/o}$ = Spreading Coefficient For Water-On-Oil
Initial Mixture Of Oil + Sea Water
$S_{o/w}$ = +
$S_{w/o}$ = -
$S_{o/w}$ = -
$S_{w/o}$ = +
Oil
Water
Oil
Oil Separates From Water Phase
Oil Remains Dispersed In Water Phase

Figure 2. Spreading coefficients indicate type of dispersion.

The Mechanism Of Dispersing Oil In Water

It can be appreciated that the spreading of the oil spill on water can be increased by surface active agents due to the lowering of the interfacial tension. The formation of either a water-in-oil or an oil-in-water emulsion is influenced by the type of surfactant. In the practical case, however, crude oil seldom reaches a state of equilibrium dictated by equation (1) due to other considerations such as increasing oil viscosity and the formation of water-in-oil emulsions such as the types called chocolate mousse.

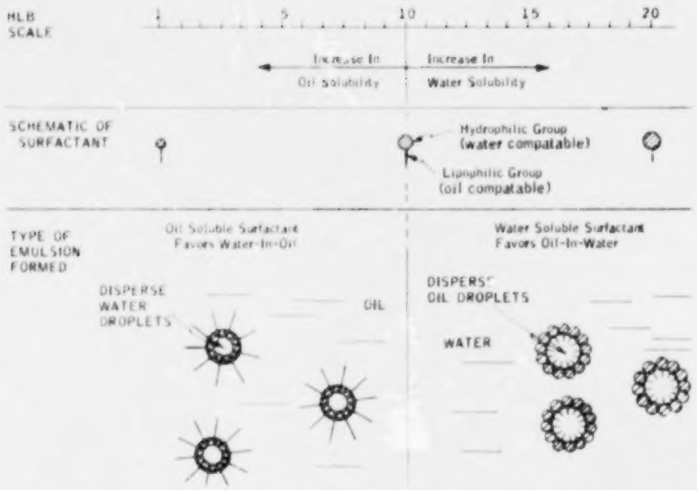
HLB SCALE
1
5
10
15
20
Increase In Oil Solubility
Increase In Water Solubility
SCHEMATIC OF SURFACTANT
Hydrophilic Group (water compatable)
Lipophilic Group (oil compatable)
TYPE OF EMULSION FORMED
Oil Soluble Surfactant Favors Water-In-Oil
Water Soluble Surfactant Favors Oil-In-Water
DISPERSE WATER DROPLETS
OIL
DISPERSE OIL DROPLETS
WATER

Figure 4. The significance of the hydrophilic-lipophilic balance of surfactant.

Further, the time required for the oil to completely film out, even if the theoretical equilibrium could be attained, is usually not available since the spill is mobile and may be beached, for example, with an onshore wind.

Therefore, in most actual applications, the dispersant is applied to an oil film that may be as thick as 1 mm or more rather than a more theoretical ultimate thickness of .0001 mm. The application of a properly selected surface active agent (chemical dispersant) reduces interfacial tension ($\gamma_{o/w}$) and enhances spreading of the oil film. More important, it promotes fine droplet formation. This can be expressed as:

$$W_K = A_{o/w} \gamma_{o/w} \qquad (2)$$

where:

W_K = mixing energy, ergs

$A_{o/w}$ = interfacial area, cm^2

$\gamma_{o/w}$ = interfacial tension, dynes/cm

Clearly then, for the same amount of mixing energy, a reduction of $\gamma_{o/w}$ will result in a corresponding increase in $A_{o/w}$.

For example, a value of interfacial tension for a gasoline-water system may be 48 dynes/cm. By equation (2), one gallon of gasoline may be dispersed into 150 μ droplets by mixing energy of 5.3 ft lbs. A 150 μ diameter gasoline droplet would have a rise velocity of 4 inches/minute in sea water. If a small concentration of surfactant, such as sodium oleate, is now added to the previously cited gasoline and water mixture, the interfacial tension would be lowered to 7 dynes/cm. Thus, by substituting this value in the preceding example calculation, the resultant dispersed droplet size for the same mixing energy would be 22 microns. The resultant settling velocity would be .086 in/min.

It can be appreciated from the above example, therefore, that the approximate seven fold decrease in interfacial tension has resulted in a greatly reduced rise velocity for the dispersed droplet. Therefore, the chemically dispersed droplet, when driven below the ocean surface by agitation, does not rise to the surface as readily.

It should be noted that the amount of mixing energy that is actually required to disperse an oil spill effectively is difficult to estimate. It is not as tractable as equation (2) would imply. A significant amount of the mixing energy is lost and merely results in agitation of the sea. Only a portion of the mixing energy is actually applied directly to the oil-water interface to promote droplet formation.

There are many surfactants that will aid in the formation of fine droplets. We have already noted that the surfactant HLB influences the efficiency of the emulsifier. However, a more subtle and less tractable requirement for an effective dispersant is the prevention of coalescence of the fine oil droplets once they are formed. This is illustrated in Figure 5 where in a volume of oil has been dispersed by a chemical surfactant and maintained in suspension by gentle bubbling of air. After 24 hours, there has been no coalescence or separation of these fine oil droplets. In the control sample, with similar volume of oil and mixing energy, the oil separated almost immediately and reformed an intact, cohesive film of oil.

In essence then, an effective dispersant must parry droplet collision physically. For example, dispersed oil may settle out in a sample bottle but even though the oil is concentrated at the surface, the droplets should not coalesce to reform an intact slick. It is this same "fendering" action that reduces the tendency of the oil droplets to stick to a solid surface. This characteristic is summarized graphically in Figure 6.

Some Practical Considerations For Dispersants

We have emphasized that oil slick dispersion is not a panacea. Dispersants have a role in oil spill cleanup and specific limits of application within that role. Like any other tool, they can be misapplied and misused. Therefore, some aspects such as the following should be considered:

1. Toxicological properties
2. Water base or petroleum base dispersant system
3. Application of mixing energy and treat rates.

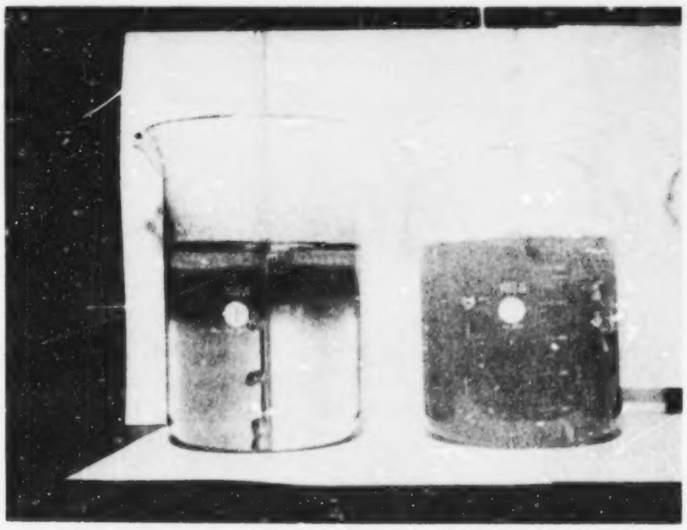

Figure 5. Effectiveness of chemical surfactant in maintaining fine droplet dispersion. Beaker at left contains no dispersant. Beaker at right contains dispersant. Air is pumped through both samples containing 1½ cc of crude oil in 3,000 cc of sea water. Note stable dispersion formed by dispersant.

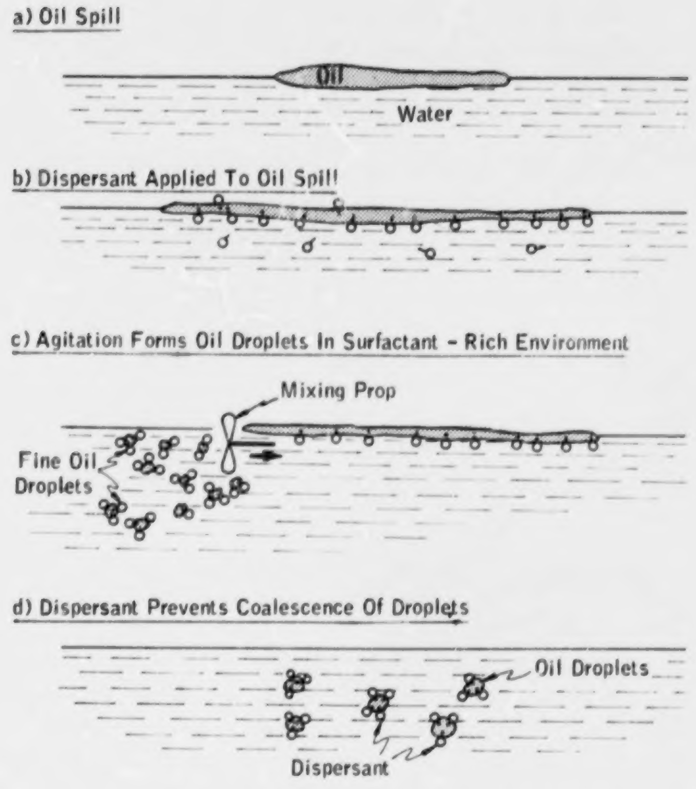
a) Oil Spill
Oil
Water
b) Dispersant Applied To Oil Spill
c) Agitation Forms Oil Droplets In Surfactant - Rich Environment
Mixing Prop
Fine Oil Droplets
d) Dispersant Prevents Coalescence Of Droplets
Oil Droplets
Dispersant

Figure 6. Dispersion of typical oil spill, viscosity <1,000 cs.

Toxicological Properties.

A comprehensive consideration of the toxicological properties of chemical dispersants is also beyond the scope of this paper. However, this has been an area of great concern. It would be academic to discuss the mechanism and benefits of chemical dispersants if they were all inherently highly toxic. The toxicity of the particular chemical dispersant is therefore a consideration that is equally as important as effectiveness. Based on some early toxicological studies of surfactants that were used to disperse oil spills, generalizations were made that all such agents were toxic and their biological effect is similar.[10]

However, suffice it to say that subsequent studies[11, 12, 13] have shown that for a particular species of marine life, TL_m values can range from 5 ppm to 3200+ ppm, depending upon the specific chemical used. TL_m is the concentration of toxicant at which 50% of the fish are unable to survive after the test exposure. Clearly then, a statement that all chemcial surfactants are, in themselves, of similar high toxicity is currently inaccurate. Although this latter concentration is greater than that which would be normally encountered, this data is still very relevant since there is always a tendency to "overtreat" and apply excessive amounts of chemical during an emergency.

Water Base Or Petroleum Base Dispersant Systems.

The surface active agent is added to a solvent–either a water or petroleum vehicle–for several reasons. The solvent improves the coverage and distribution of the surfactant onto the oil spill. It reduces viscosity and thereby makes application easier. By inspection of the prior discussion, it can be appreciated that the critical component is the surface active agent itself, however, and not the type of solvent. It should be noted though that whether the dispersant system utilizes a water solvent with a predominantly water-compatible surfactant or a petroleum solvent with the converse, it does influence the method of application.

For example, a common method of dispersant application is by the water eductor method. A controlled amount of dispersant is educted into a water stream such as a fire hose. This water jet is an effective vehicle or carrier for the dispersant and provides good coverage in treating the slick. Figure 7 illustrates this type of application wherein an aqueous solution of a dispersant is educted into the fire main system and then applied to the oil spill by means of a spray boom. The boat's bow wake and propeller provide the needed mixing energy for dispersing the oil slick.

This application procedure however, while compatible with a water base system, is imcompatible with a petroleum base system. This is because a dispersion of the petroleum

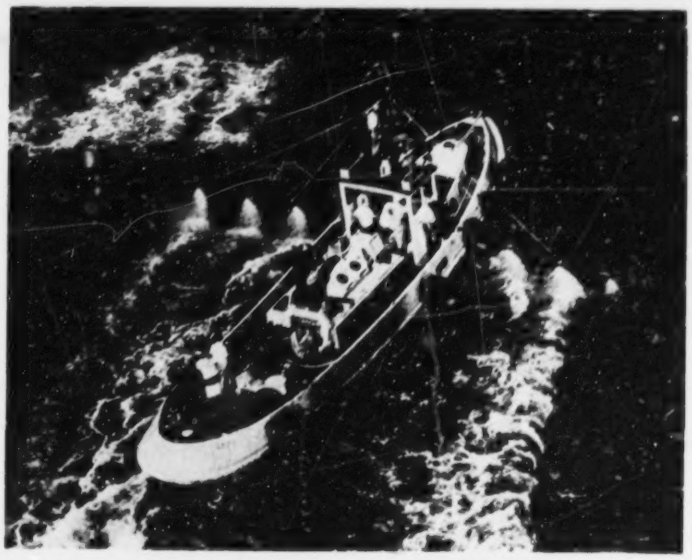

Figure 7. Application of chemical dispersant to oil slick.

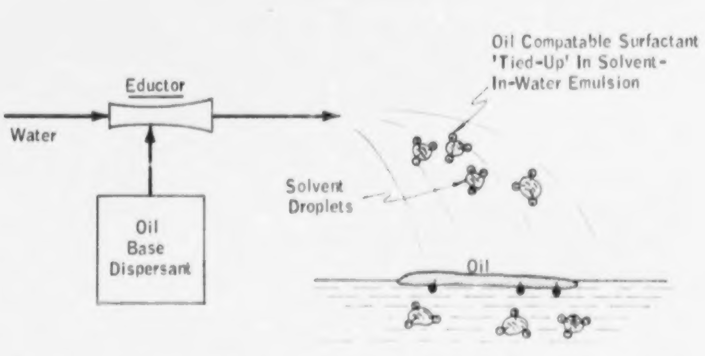
Eductor
Water Stream
Water
Water Compatable Surfactant
Water Base Dispersant
Oil
Oil Compatable Surfactant 'Tied-Up' In Solvent-In-Water Emulsion
Eductor
Water
Solvent Droplets
Oil Base Dispersant
Oil

Figure 8. Behavior of oil base and water base surfactant when applied by water eduction method.

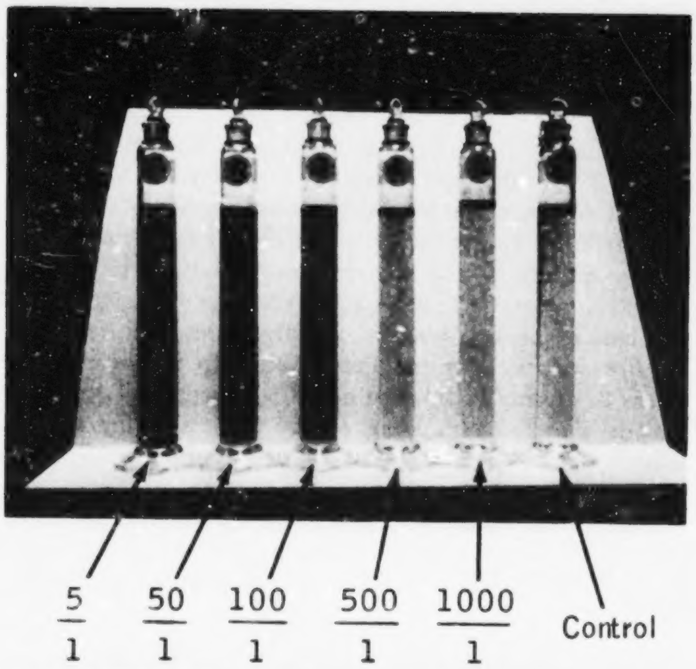

Figure 9. Effect of dispersant concentration on dispersion of So. La. crude in sea water. Concentrations shown are parts of oil/part dispersant.

solvent-in-water is formed as soon as the surfactant system is educted into the water stream. As illustrated in Figure 8, this accounts for the milky white appearance of the water after such applications. In this state, as graphically shown in Figure 8, it is difficult for the surfactant to transfer from its thermodynamically stable location at the petroleum solvent-water interface to the oil spill-sea water interface. Therefore, for a petroleum base system, neat application of the chemical directly onto the oil slick is a more effective application method.

This aspect also illustrates the dilema of applying any "standard" laboratory test to determine dispersant effectiveness. Once factors such as mixing energy and heat versus water eduction application method are fixed, one system may be favored over another in some test procedures.

Application Of Mixing Energy And Treat Ratios

The prompt application of mixing energy after the dispersant has been applied is particularly important for a water base system. In essence, small oil droplets must be produced while the immediate water environment is surfactant-rich.

Mixing energy, as well as the methods of application previously discussed, influence the treat ratio:

$$\frac{\text{parts of oil}}{\text{parts of dispersant required}}$$

Primarily, the treat ratio–in essence, the efficiency of the surfactant to disperse oil–is determined by the molecular structure of the surfactant. However, how effectively it is applied then determines what percentage of its theoretical dispersing capability is realized. Figure 9 illustrates that under ideal laboratory conditions, a treat ratio of 100 parts of oil to one part of a particular dispersant is effective. However, in practice, loss of chemical into the water environment and overtreating tend to reduce these theoretical treat ratios.

Other factors influence the treat ratio. Higher treat ratios are attained, as expected, on larger spills since losses of the chemical at the edge of the slick and fixed losses of chemical in the spray system, etc., are relatively smaller.

Finally, the viscosity of the spilled oil is an important consideration. Obviously, in the treatment of liquid-liquid interfacial behavior, it is requisite that both the oil and water are liquid. Some dispersants can become marginally effective for semi-solid oils. This is illustrated by Figure 10 where it can be seen that at a level of 1000 centistokes (a viscosity of 1000 centistokes represents a very slow pouring, highly viscous liquid) a particular dispersant becomes marginally effective. It is of interest to note, however, the >90% of the cargoes transported by tankers are well below this value of viscosity even when spilled in cold water.

In summary, concerning the incentive and effects of dispersing oil, it must be appreciated that we are not dealing with a comparison of a clean water environment versus a marine environment with chemically dispersed oil droplets. Rather, the choice is between a large, damaging, cohesive oil slick–which we are unable to remove from the sea–versus chemically dispersed oil droplets. One must objectively consider all available data from the many ongoing studies in this area to select the least objectionable situation. If left untreated, the naturally occurring surfactants in most crude oils can produce a highly viscous water-in-oil emulsion. This compact agglomerate of oil and water can be resolved and countered by use of man-made surfactants (dispersants). Whether applied to an intact oil film or the above noted emulsion, the dispersant promotes the formation of fine oil droplets in water, thereby removing the potentially damaging volume of oil from the surface. Although not overly complex, it can be seen that the selection of a chemical for use as a dispersant and its method of application does involve some first principles of surface behavior.

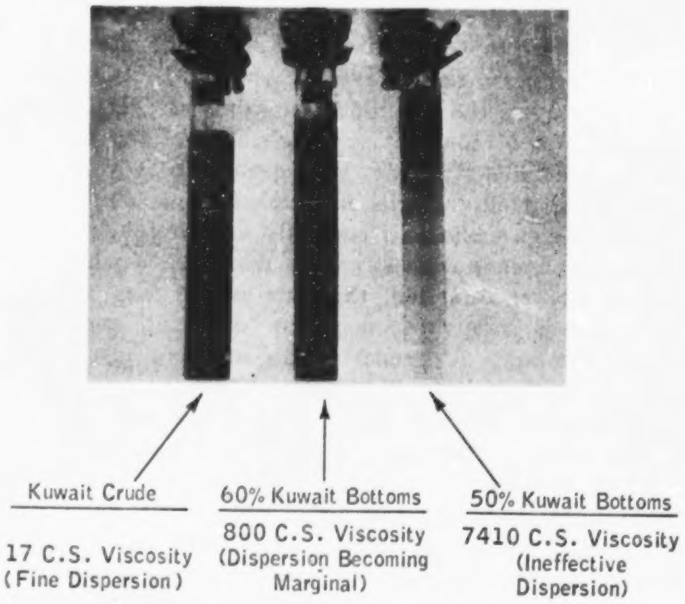
Kuwait Crude
17 C.S. Viscosity (Fine Dispersion)
60% Kuwait Bottoms
800 C.S. Viscosity (Dispersion Becoming Marginal)
50% Kuwait Bottoms
7410 C.S. Viscosity (Ineffective Dispersion)

Figure 10. Effect of oil viscosity on stability of dispersion. All samples were treated with one part dispersant per 10 parts of oil and given similar agitation.

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Standard Methods For Determination Of Relative Toxicity Of Oil Dispersants And Mixtures Of Dispersants And Various Oils To Aquatic Organisms

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Abstract

It is the policy of the Federal Water Pollution Control Administration of the U. S. Department of the Interior that the relative toxicity of all chemical dispersants, both alone and in combination with oil, will be determined prior to their use for the dispersion of oil spills, and the cleaning of beaches and shore installations. Data on the relative toxicity of these materials alone–and when mixed with oil–provide the basis for the effective selection of those materials least toxic to aquatic life and for recommending or prohibiting their use.

The Department takes the position that it is the responsibility of the manufacturer of such products to provide for their product alone and in oil mixture accurate tolerance limit values based on standard short-term bioassays with designated test organisms. The standard bioassay procedure used will be the one recommended by the FWPCA. This procedure is solely for the purpose of providing data which will indicate relative toxicity of dispersants and oil dispersant mixtures. These standard tests do not indicate the long-term toxicity of these materials to aquatic organisms, safe levels for the aquatic biota or for humans, nor do they constitute an endorsement of any material by the FWPCA.

General Bioassay Procedures

Bioassay methods for the determination of the short-term toxicity of various material to fishes have been used for many years. Descriptions of such methods have been included in the eleventh and subsequent editions of "Standard Methods for the Examination of Water and Wastewaters."[1] The bioassay methods recommended herewith are based on these standard methods but they are modified to meet the special problems arising in the use of fishes and of test organisms other than fish in the bioassay of oil dispersants and mixtures of oil dispersants and different petroleum products.

Because of special problems arising in the bioassay of oil and oil dispersant mixtures, and the necessity for the comparability of results, certain procedures described in Standard Methods must be made specific and standardized. These include special bioassay methods for organisms other than fish and the standardization of certain elements and conditions of the test such as the test species, mixing and agitation, dilution water, aeration, DO concentrations, temperature, pH and salinity.

Oil used in these bioassays must be as it comes from the well or as it is in the oil tankers. Small portions used in bioassays must be shipped and stored in sealed containers to prevent the loss of volatiles and other changes. For ease in handling and use, it is recommended that 100 ml glass containers be used and a minimum of 40 containers of each grade or kind of oil under test be available.

In order to insure comparable results, oils to be used in the bioassay tests will be packaged and sealed at a central location designated by the Department and shipped on request to those carrying out the bioassays. Gastight calibrated syringes of 0.001, 0.01, 0.1, 1, 5, 10, 30 and 60 ml capacity should be used to add the calculated amounts of the test materials to each test jar. These should have teflon tipped plungers. Unused oil in each open container should be disposed of upon the completion of the dosing to prevent its use at a later date when it has lost its volatiles. All tests in a bioassay series should be run with oil from the same container and with organisms from the same group collected or secured from the same source. For each species

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[1] Superior numbers refer to literature references at conclusion of text.

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under study, specimens should be of the same age and size range.

Dispersants used for bioassays should be kept sealed when in storage. The ratio of dispersant under test to the oil being tested should be in accordance with the manufacturer's recommendation. Generally, the ratio is one to ten by volume.

In order to insure consistency in the assays carried out by different workers and to detect any changes in the condition of the test organisms which might lead to different results, there shall be carried out in addition to the usual control tests, reference bioassays made with reagent-grade dodecyl sodium sulfate, commonly known as sodium lauryl sulfate. A stock solution of dodecyl sodium sulfate (DSS) is provided by preparing a solution having 1 gm of DSS per 500 ml of solution. This solution made with either the fresh or salt water formula should be prepared immediately prior to use. When all conditions of the bioassay are met, and the outlined tests carried out, results of bioassays made in different areas and by different investigators will be comparable and serve to indicate the relative toxicity of different dispersants and dispersant-oil mixtures. Results of all bioassays should be expressed in TL50 values.

Bioassays of each product under study will include tests to determine the median tolerance limit of the dispersant alone and in mixtures with oil in the ratio recommended for use by the manufacturer with each of two crude oils and two fuel oils recommended by the Department for use in the bioassays.

Bioassay Procedures Using Fish

Ninety-six hour static bioassays will be used for these tests. These will be carried out in general as prescribed in "Standard Methods for the Examination of Water and Wastewaters" as to replications, weight and number of test fishes, acclimation, transfer, feeding, calculation of TL values and reporting of results. However, depth and volume of water, mixing, temperature, method and amount of aeration and agitation, DO, composition of dilution water, pH and salinity, reference standard and test fish will be standardized as set forth herein in order to insure comparability of results.

Tests will be carried out in 4 liter (approximately 1 gallon) glass jars measuring approximately 22.5 cm high, 15 cm in diameter, and 11 cm in diameter at the mouth. The jars are to have screw top lids and be lined with a nontoxic plastic film. In carrying out the test, 2 liters of the synthetic dilution water aerated to saturation with DO will be added to each of the jars. For ease and accuracy in adding the 2 liters, an automatic dispensing pipette (Figure 1) of 2 liters capacity is recommended.

Test fish for use in the bioassays must be acclimated to the selected temperature and salinity for a period of 10-14 days before being used for the bioassays to determine relative toxicity. Groups of fishes having more than 20 per cent mortality during the first 48 hours and more than 5 per cent thereafter should be discarded. During acclimation, all species are fed a balanced diet. A homogenate of ground clam, 80 per cent by weight; dog biscuit or fish meal, eight per cent; water, 10 per cent; and gum arabic crystals, two per cent, has been found to be satisfactory. This diet–or another wet formulation selected for use–should be frozen immediately after preparation and thawed at room temperature before feeding. Unused thawed portions are discarded daily. These precautions are not necessary if a fresh food or fish meal is used. The fish are fed twice daily to saturation but are not fed for 48 hours prior to or during the bioassay test. Only those organisms which feed actively and appear to be healthy are used in the bioassays. Any individuals injured or dropped while handling must be discarded. During acclimation of marine species, water temperatures should reach a final level of 20°C ± 1°C, pH

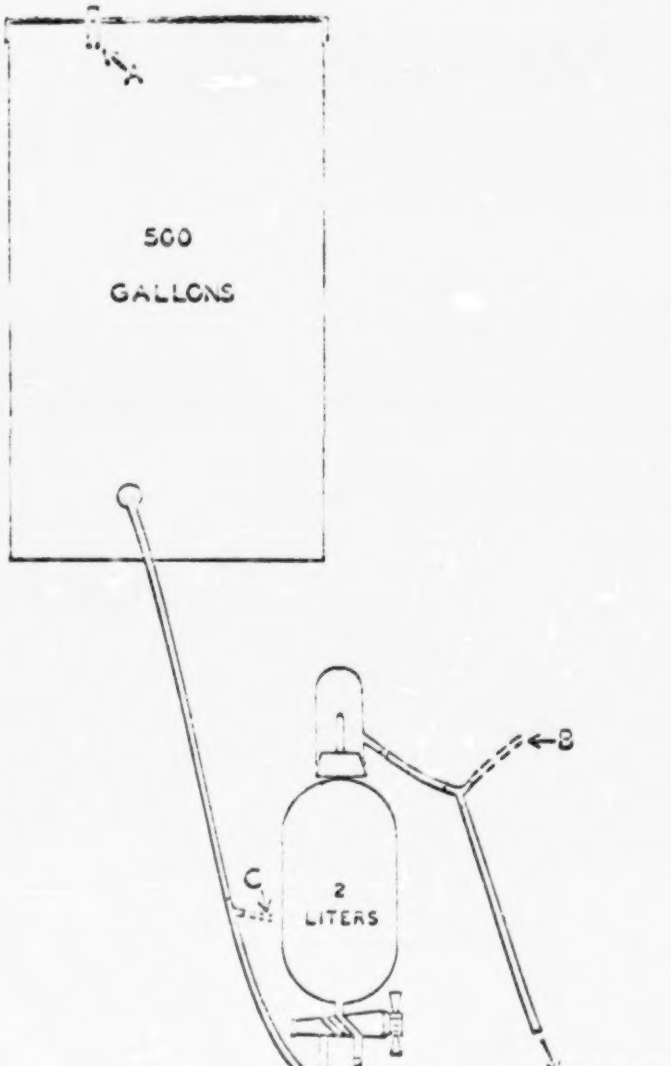

Figure 1. Schematic diagram of automatic dispensing pipette system utilizing in bioassay procedure. Inflow A is from large holding reservoir. Overflow B is from other units in series. Inflow C is to other units.

should reach the level of 8.0 with a variation of ± 0.1 unit. Salinity should be brought down to a level of 20 ppt ± 0.5 ppt. Fresh water species should be acclimated to a water temperature of 25°C ± 1°C and a pH of 7.5 to 7.8. Oxygen levels should be kept above 4 ppm, preferably between 5-6 during the acclimation period. All tests in a series should be run with the same batch of oil and with organisms from the same group. Specimens should be of a uniform size and age and of the same species.

Standard Fish. Freshwater–Fathead Minnow *(Pimephales promelas)*; saltwater–Mummichog *(Fundulus heteroclitus)*.

Standard Dilution Water. Because large quantities of dilution water will be used in these tests, it is desirable to prepare the synthetic water in large batches to insure uniformity and constant conditions for the various tests. To prevent contamination, the synthetic standard dilution water should be prepared and stored in fiberglass containers of suitable size.

Standard Freshwater Formulation. The standard freshwater shall be prepared as follows: Bubble CO_2 through 10 liters of distilled water containing 2.1 gms of $CaCO_3$ in order to convert it to a clear solution of $Ca(HCO_3)_2$. Dilute this solution with 20 liters of distilled water and add 30 ml of a mixed salt solution. Any multiple of these volumes and weights may be used to secure desired volumes of the standard water. This mixed salt solution is prepared by dissolving 23.4 gms of NaCl, 73.9 gms $MgSO_4 \cdot 7H_2O$ and 4.4 gms K_2SO_4 in distilled water and making up to one liter.

This produces a water which is very close in dissolved materials to the average natural stream waters of the U. S. In the preparation of the standard water, care must be given to the quality of the distilled water. All distilled water used should be from a glass still or from a tin-lined still to insure the absence of metal ions. The pH of this water shall be in the range of 7.6 to 7.8. Adjustments are made by the addition or removal of CO_2.

Standard Seawater Formulation. For the preparation of the standard seawater, technical grade salts are mixed with distilled or demineralized water in the order and quantities listed below. It is important that the ingredients be added in the order listed and that each ingredient be dissolved before another is added. This is best accomplished by a constant stirring in the course of the preparation. To 900 liters of deionized or distilled water, add the following ingredients:

20 gm $SrCl_2 \cdot 6H_2O$ (reagent grade if technical grade is not available);
30 gm H_3BO_3; 100 gm KBr; 700 gm KCl; 1100 gm $CaCl_2 \cdot 2H_2O$; 4000 gm Na_2SO_4;
5000 gm $MgCl_2 \cdot 6H_2O$; 23500 gm NaCl; 20 gm $Na_2SiO_3 \cdot 9H_2O$; 200 gm $NaHCO_3$;
3.0 gm Ethylene diamine tetraacetate (EDTA-tetra sodium salt)(reagent grade if technical grade not available).

Make up to 1000 liters by the addition of distilled or demineralized water. The pH should now be 8.0 ± 0.1. The desired salinity of 20 ppt ± 0.5 ppt is attained at time of use by diluting with distilled or demineralized water.

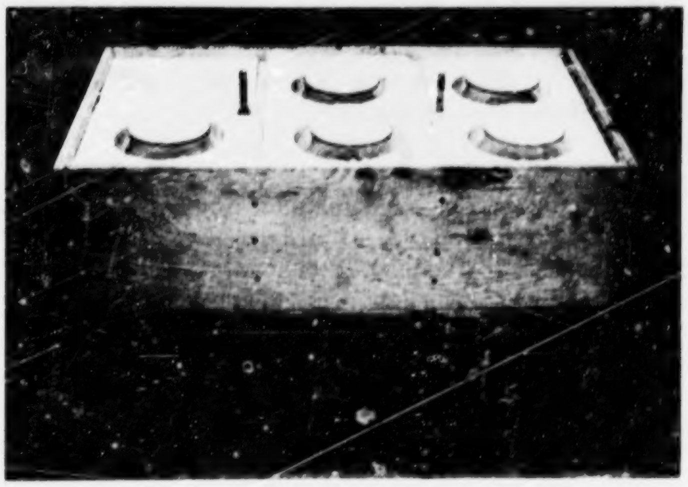

Figure 2. Reciprocal shaker with platform to hold bioassay jars.

Temperatures. When bioassays are made to determine the comparative toxicity of oil dispersants and mixtures of dispersants and various petroleum products, all tests must be carried out at the same recommended temperature.

For these bioassays, temperatures of test solution shall be 25°C ± 1°C for fresh water species and 20°C ± 1°C for marine species.

Mixing the Test Material in the Dilution Water. The test jars containing 2 liters of the standard water are placed on the reciprocal shaker (Figure 2). The petroleum product under test may be added, in the desired amount with calibrated syringe, directly to each test jar. Then the appropriate amount of the dispersant-standard water stock is added with a pipette or the pure dispersant by means of a calibrated syringe. The test jars are then tightly capped and shaken for 5 minutes at approximately 315 to 333 three-fourths in. strokes per minute on a reciprocal shaker.

The shaker platform should be adapted to firmly hold six of the bioassay jars (Figure 2). At the completion of

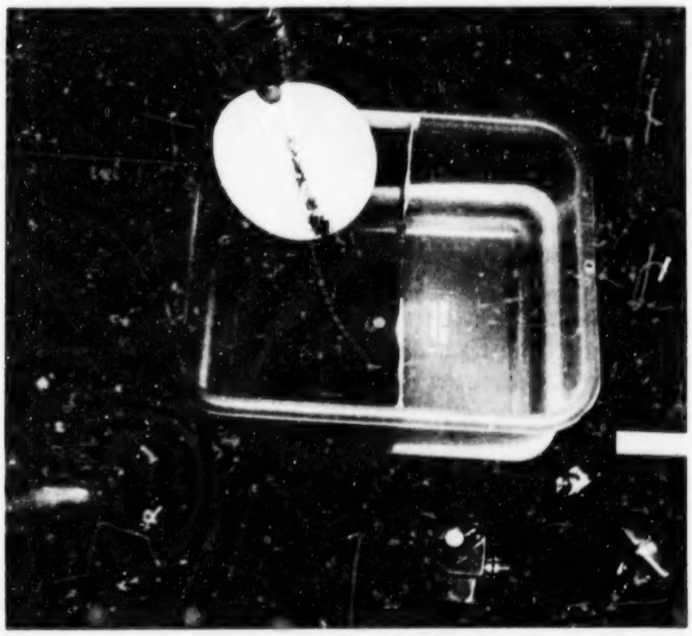

Figure 3. Adding Artemia eggs (on the filter paper) to the hatching chamber.

shaking, the jars are moved from the shaker, placed in the constant temperature water bath or room, the lids are removed and the two test organisms (fish) added. All operations are carried on at 20°C ± 1°C for marine species and 25°C ± 1°C for the fresh water species.

Dissolved Oxygen and Aeration. Since oils and dispersants contain volatile materials, many of which are toxic, and since the toxicity of some water soluble fractions of oil and its degradation products are modified by oxidation, special care must be used in the oxygenation of test solutions. Aeration to provide DO and mixing is initiated after the test organisms are added. The dissolved oxygen content of test solutions must not drop below 4 ppm.

In order to limit the removal of volatiles, it is desirable to keep aeration at a minimum and aerate only enough so as to keep the DO concentration between 4 and 5 ppm. Aeration should be at the rate of 100 ± 15 bubbles of air per minute supplied from a 1 ml serological pipette having an inside diameter of 1 mm. At this rate and with the proper weight of fish, DO concentration can be maintained slightly above 4 ppm over a 96-hour period. Dissolved oxygen measurements must be taken at least daily according to "Standard Methods for the Examination of Water and Wastewaters."

Recording Data and Calculating Results. Dead fish are recorded and removed daily. At the end of the 96-hour period, the assays are terminated and the TL50 values determined as described in "Standard Methods for the Examination of Water and Wastewaters." Results are expressed in ml of the dispersant and of dispersant and oil mixture per liter of liquid in the test containers.

Bioassay Procedures Using Oyster Larvae

Production of Test Organisms. Organisms to be used in these tests are the larvae of the oyster *(Crassostrea virginica)* from the 0 to the 48-hour stage, i.e., from the period of hatching to 48 hours thereafter. Under the conditions of the bioassay, the oyster larvae should develop to the straight hinge stage during this 48-hour period.

This test necessitates an available supply of newly hatched oyster larvae so that the tests can be carried on from the fertilization of the egg to the 48-hour stage.

To insure a continuous supply of eggs, sufficient numbers of adult oysters should be held in suitable containers at temperatures below 15°C, preferably in a range of 5 to 7°C, or lower, so that they will be available over longer periods. As larvae are needed, a number of these adult oysters are transferred to other containers and held at 20°C for development of the sex products. When fertilized eggs are needed, approximately twelve of these sexually matured and ripened oysters are placed in glass spawning dishes of 1 liter capacity.

It has been found satisfactory to use dishes of about 10 x 25 x 10 cm. These oysters are covered with the artificial seawater developed for this test and described herein. These spawning dishes are then placed in a water bath and raised from the holding temperature of 20°C to a temperature of 27-28°C. Often this rise in temperature is sufficient stimulation to trigger spawning, but at times it may be necessary to artificially induce spawning in at least a portion of the specimens.

If one or more individuals spawn due to the increase in temperature, a small amount of the gametes are taken and added to the other jars to induce the spawning. If none of the specimens spawn, a ripe and mature oyster should be opened and the material from the gonads taken and added to the spawning dishes in order to induce spawning. After spawning, 2 ml of sperm suspension from one of the spawning dishes containing a male is added to each of the spawning containers, in which females have depositied eggs, for the fertilization of the eggs.

The female oysters are then removed from each of the spawning dishes and the liter of water containing the eggs and sperm are passed through a 54 micron nylon mesh screen into a glass beaker. This screen serves to remove debris and feces which may be present.

After allowing the suspension to stand for thirty minutes to insure fertilization and settling, the excess water is decanted off and the fertilized eggs are removed by means of a Pasteur pipette having an opening of 1 mm. These eggs are then concentrated into one container and artificial seawater added sufficient so that the resulting suspension, when mixed, contains about 20 eggs/ml. The eggs are then without delay transferred in 1 ml of the suspension (20 eggs) to the containers used in the bioassays which already contain the test solutions.

Standard Artificial Seawater. The artificial seawater used in bioassays with oyster larvae is prepared in the same manner and is essentially the same water used in the fish bioassays. However, much smaller quantities are needed, and the following formulation is suggested for the making of smaller volumes of this water.

In the formulation of this water, technical grade salts are mixed with distilled or demineralized water in the orders and quantities listed below. The final water should have a salinity of 22 o/oo. This is achieved by diluting the mixture down with distilled or demineralized water. Final water should have pH adjusted to 8.0 - 8.2 when necessary by the addition of $NaHCO_3$. Before this water is used, it is filtered through a .22 micron Millipore filter under vacuum. The formulation is as follows:

To 900 ml of distilled water, add in the order given:

$SrCl_2 \cdot 6H_2O$	0.02 gm	$MgCl_2 \cdot 6H_2O$	10.00 gm
H_3BO_3	0.03 gm	NaCl	23.50 gm
KBr	0.10 gm	$Na_2SiO_3 \cdot 9H_2O$	0.02 gm
KCl	0.70 gm	$NaHCO_3$	0.20 gm
$CaCl_2 \cdot 2H_2O$	1.10 gm	Distilled H_2O to make	1 liter
Na_2SO_4	4.00 gm		

To each liter of the above artificial seawater, add 3 mg of EDTA (tetra-Na-salt) to mitigate toxicity of trace metal impurities. This solution is made to the desired salinity of 22 o/oo by the addition of demineralized water.

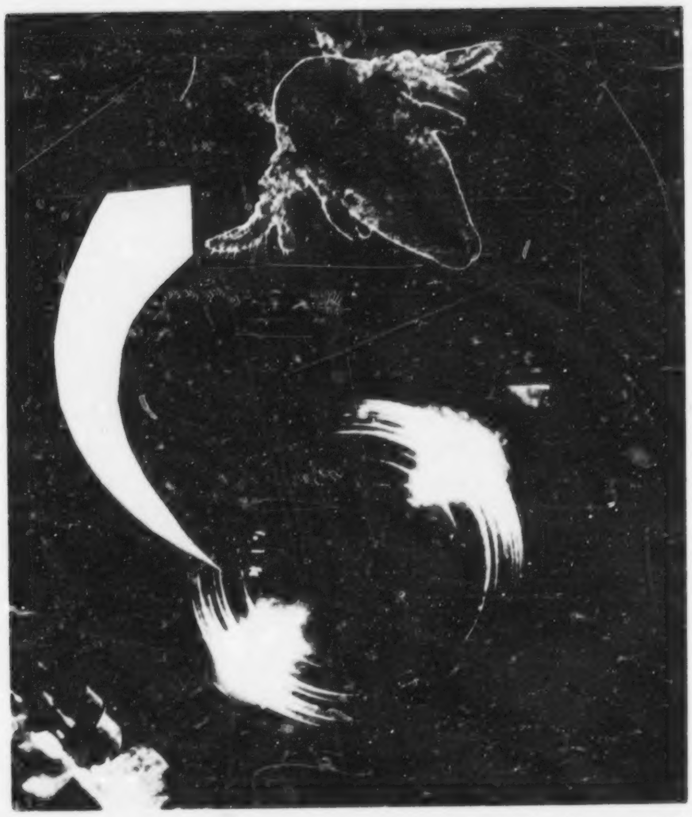

Figure 4. Twenty-four hour Artemia salina nauplei in the test dish (bottom), and magnified 100 times (top).

Preparation of Test Toxicants. For the determination of the relative toxicity of dispersants and oil-dispersant mixtures to oyster larvae, test solutions should be prepared in the following manner: (1) Blending or mixing is to be accomplished by an electric blender having speeds of 10,000 to 20,000 rpm or less, a stainless steel cutting assembly and a 1 liter borosilicate jar. It is desirable to do the blending at speeds below 10,000 rpm in order to minimize foaming. (2) For the dispersant test solution, add 550 ml of the standard seawater to the jar, then by means of a gas-tight μl calibrated glass syringe with a teflon-tipped plunger, add .55 ml of the dispersant and mix for 5 seconds. This serves as the stock solution for the dispersant when tested alone. (3) For the dispersant-oil mixture, add 550 ml of the standard seawater to the mixing jar. While the blender is in operation at the lowest speed but not more than 10,000 rpm, add 0.5 ml of the oil under study by means of a calibrated μl syringe with teflon-tipped plunger and then 0.05 ml of the dispersant as indicated above. Blend for 5 seconds after addition of dispersant. These additions provide test solutions of the dispersant and the oil-dispersant mixture at a concentration of 1000 ppm of dispersant and oil-dispersant combination respectively and in a ratio of dispersant to oil of 1 to 10.

Test Procedure. The bioassay tests are carried out by the use of covered petri dishes having a diameter of 60 mm and a depth of 15 mm. These dishes should be properly labeled in advance and prepared with the necessary amount of the standard artificial seawater and the test solution so that the test organisms may be added directly to the petri dishes. The dispersant or oil-dispersant test mixture is added to the petri dishes immediately after mixing.

Each test will consist of 5 replications of each concentration of the material under study. Concentrations of the material used are to correspond to quarter points in the logarithmic series. For example, concentrations might be 10, 18, 32, 56 and 100 ppm. In addition to these 5 series of test toxicants, a control series of 5 dishes and a standard reference series set up of 5 different concentrations are needed. This makes 35 test containers in all.

Immediately after the test solution of the dispersant or oil-dispersant solution is prepared, using a syringe of appropriate size, draw up the necessary amount of test solution and disperse into each of the 5 containers for each concentration. If the series of 5 concentrations are 10, 18, 32, 56 and 100 ppm, the amount of the test solution to be added to each of the 5 replications of each test concentration in the order of the concentrations listed above would be as follows: 1, 1.8, 3.2, 5.6 and 10 ml.

Each time a syringe is to be filled for dispensing to the series of test containers, start the mixer and withdraw the desired amount in the appropriate syringe while the mixer is in operation. Turn off immediately after the sample is taken in order to limit the loss of volatiles.

The concentration of the reference standard to be used in each series of bioassay tests should be determined by exploratory tests before the full-scale test is set up. After addition of the required amounts of the test oil and dispersant or dispersant mixture, add standard artificial seawater to each test container to bring the total volume up to 99 ml, then from the egg and seawater suspension (which has been diluted so that there are 20 eggs per ml) with the use of a pipette, transfer 1 ml into each of the test containers. The total volume in each test container is then 100 ml.

The blender must be washed thoroughly after each use and the above procedures repeated for each test series. The suggested procedure for washing is described in the *Artemia* tests.

Recording Data and Calculating Results. At the end of the 48-hour exposure, the bioassays are discontinued and evaluated on the basis of shell formation using the full-shell criteria of Woelk.[2] Normal larvae are those which are fully shelled regardless of their size and shape. Those with no shells or partial shells are considered as abnormal. The larvae from each of the test dishes are counted and examined and the number of full-shelled individuals recorded for each concentration. These numbers are plotted as percentages of normal individuals on semi-log paper and the TL50 value is obtained as described in "Standard Methods for the Examination of Water and Wastewaters." All results of these studies should be expressed as the 48-hour TL50 value which will serve to indicate the relative toxicity of different dispersant and oil-dispersant mixtures.

Bioassay Procedures Using the Brine Shrimp

Because dried eggs of the brine shrimp *(Artemia salina)* are available throughout the country and can be stored without maintenance for long periods of time, this organism is a very good one for use in bioassays to determine the relative toxicity of dispersants and oil dispersant mixtures. Because artificial seawater is used for bioassays with this organism, these tests can be carried out anywhere in the country with a minimum of space and equipment.

Standard Seawater Formulation. The artificial seawater formula to be used in bioassays with *Artemia* is the same as that specified for the oyster larvae.

Other Test Conditions. Bioassays using *Artemia* are to be carried out at 20°C. Artificial seawater used in the test chambers should be adjusted to pH 8.0 - 8.2. Salinity of the standard artificial seawater for these tests should be 30 o/oo. This is attained by diluting the standard formulated artificial seawater with distilled or demineralized water.

Dissolved Oxygen. Bioassay tests will be carried out in 3.5 x 1.5 in. Carolina culture dishes. The surface area of the test solution exposed in relation to volume is so large that dissolved oxygen is not a problem. Oxygen content remains high throughout the assay because of the small quantity of test substances added and the low oxygen demand of organisms in each dish.

Providing Experimental Organisms. When conducting bioassays, it is essential to have ready an adequate number of experimental organisms of the correct age and size. To insure uniformity of test organisms, eggs should be secured from the San Francisco Bay area. Since the eggs of *Artemia* may be kept dessicated for long periods in a viable state, required numbers of the organism can be secured at any time for use in the bioassay tests through the use of proper hatching procedures.

All hatched *Artemia* are of the same age and physiological history. A rectangualr, plastic, glass or enamel tray having at least 200 square inches of bottom surface is suitable for the hatching of *Artemia* eggs.

Divide this tray into two parts by a partition which extends from the top down to about three-quarters to half an inch from the bottom. This partition may be of any opaque, biologically inert material. It has been found that a pasteboard strip, sealed with paraffin wrapping, is satisfactory. Raise one end of the tray about one-half inch and add 3 liters of the standard seawater formulation. Spread (Figure 3) 0.5 gram of brine shrimp eggs in the shallow end of the tray. Cover this end of the tray with a piece of cardboard to keep the eggs in darkness until hatching is complete. About 20 hours after the eggs hatch, direct a narrow beam of light across the other portion of the tray. Since the brine shrimp are phototactic, they will swim beneath the partition into the illuminated end of the chamber and congregate in the beam of light (Figure 4), which makes them easy to collect.

Collect the *Artemia* concentrated in the beam of light by the use of a collecting pipette or siphon. Transfer them to a container having a small amount of the artificial seawater. It is more convenient to handle and transfer these animals with a small pipette connected to a 12-in. rubber tube and mouthpiece (Figures 3 and 7).

In order to have the necessary *Artemia* ready for the study, transfer 20 *Artemia* into each of 35 small beakers each containing 20 mls of artificial seawater. These 35 batches of *Artemia* are then held until they are 24-hours old at which time they are placed in the respective series of five test concentrations set up for the bioassay.

Bioassay Procedures. In studies to determine the median tolerance limit of *Artemia* to oil dispersants (or mixtures of these dispersants and various oils) five different concentrations of each material should be used. These concentrations should be the quarter points of a logarithmic series as described for all bioassay procedures in "Standard Methods for the Examination of Water and Wastewaters."

Each bioassay for a particular material and for the reference standard would consist of the five different concentrations (each with five replications) and a control with five replications, or a total of thirty-five exposure chambers. The reference standard, sodium dodecyl sulfate, is used in order to determine whether results obtained are comparable with those of other tests. The reference standard serves primarily to detect any changes in the test organisms. All dishes should be prepared in advance with the appropriate volumes of standard seawater and dispersant or dispersant and oil mixture so they are ready when test animals are just 24 hours old.

Test Chambers and Solutions. Before each assay, process all required glassware by immersing it in cleaning solution, (70 per cent alcohol and 30 per cent sodium hydroxide) for at least 30 minutes. Rinse thoroughly in tap water, scrub with hot detergent solution and rinse three times with hot tap water, followed by three rinses of distilled or demineralized water. Oven or air dry glassware in a reasonably dust free atmosphere.

Preparation of Test Concentrations. For these studies, test solutions for the determination of the relative toxicity of dispersants and dispersant and oil mixtures are prepared as follows: (1) Blending or mixing is to be accomplished by an electric blender having speeds of 10,000 to 20,000 rpm or less, a stainless steel cutting assembly and one liter borosilicate jar. It is desirable to do the blending at speeds below 10,000 rpm in order to minimize foaming. (2) For the dispersant test solution, add 550 ml of the standard seawater to the jar, then by means of a gas-tight μl calibrated glass syringe with a teflon-tipped plunger, add .55 ml of the dispersant and mix for five seconds. This is the stock solution for the dispersant when tested alone. (3) For the dispersant-oil mixture, add 550 ml of the standard seawater to the mixing jar. While the blender is in operation, add 0.5 ml (Figure 5) of the oil under study by means of calibrated μl syringe with teflon-tipped plunger and then 0.05 ml of the dispersant as indicated above. Blend for five seconds after addition of dispersant. These additions provide test solutions of the dispersant and the oil-dispersant mixture at a concentration of 1000 rpm of dispersant and oil-dispersant combination respectively and in a ratio of dispersant to oil of one to ten.

For carrying out the tests, 35 Carolina culture dishes, suitably labeled, having a dimension of 3½ x 1½ in. should be prepared in advance and be ready for the introduction of the dispersant or the oil-dispersant stock solution immediately after mixing.

Each test will consist of 5 replications of each concentration of the material under study. Concentrations of the materials are to be at quarter points in a logarithmic series; for example, concentration studies might be 10 ppm, 18 ppm, 32 ppm, 56 ppm and 100 ppm. In addition to these 5 series, a control series of 5 dishes and a standard reference

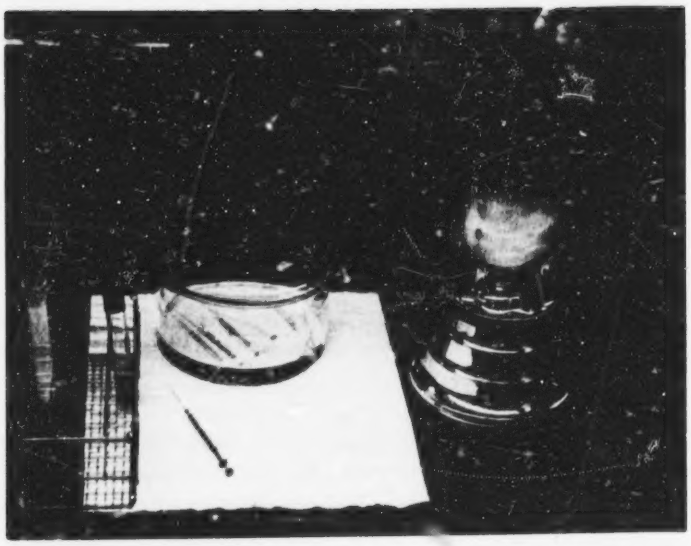

Figure 5. Adding dispersant to the assay medium by displacement from a microliter syringe.

series set up at 5 different concentrations are needed. This makes 35 dishes in all.

Immediately after the test solution of the dispersant or oil-dispersant solution is prepared, using a syringe of appropriate size, draw up the necessary amount of test solution and dispense into each of the five containers in each series. If the series of five concentrations which are to be tested are 10, 18, 32, 56 and 100 ppm, the amount of the test concentration in the order of the concentrations listed above would be as follows: 1, 1.8, 3.2, 5.6 and 10 ml.

Each time a syringe is to be filled for dispensing to the series of test containers, start the mixer and withdraw the desired amount in the appropriate syringe while the mixer is in operation. Turn off immediately after the sample is taken to limit the loss of volatiles.

The concentration of reference standard to be used in each of the five different concentrations should be determined by exploratory tests before the full-scale test is set up. After addition of the required amounts of the test oil and dispersant or dispersant mixture, bring the volume of liquid in each of the test containers up to 80 ml with the artificial seawater. To insure keeping each of the series separate, designate on each lid of the test containers the date, the material under test and its concentration. These operations should be carried out at 20°C± 1°C.

When the desired concentrations are prepared, gently release into each dish the 20 test animals (previously transferred into 20 ml of medium) as shown in Figure 6. This provides a volume of 100 ml in each test chamber. A pair of standard cover glass forceps with flat, bent ends are an ideal tool for handling and tipping the small beaker without risk of contaminating the medium.

The blender must be washed thoroughly after each use and the above procedures repeated for each series of tests. The following is a suggested method of washing:

1. Pour a strong solution of laboratory detergent into the blender to cover the blades.
2. Fill the container about ½ of its volume with hot tap water.
3. Operate the blender for about 30 seconds at high speed.
4. Remove and rinse twice with hot tap water, mixing each rinse for five seconds at high speed.
5. Rinse twice with distilled water, again mixing the first rinse.

Exposure. After adding the test animals, incubate the assay dishes at 20°C for 48 hours (Figure 7). Fluctuations of ± 1°C are acceptable during incubation. Recommended lighting is 200 ft-c of diffused, constant, fluorescent illumination coming from beneath the culture dishes during incubation (Figure 7). Because *Artemia* are phototactic, bottom lighting should keep them from direct contact with the oil that sometimes layers on top.

Observations. Terminate the test after 48 hours of incubation in the oil and dispersant mixture. To count the dead animals accurately and with relative ease, place the test dishes on a black surface. Most dead *Artemia* will be on the bottom of the test dish and can be seen readily against the black background when a narrow beam of light is held parallel to the bottom of the dish (Figure 4). However, also search the top of the liquid for *Artemia* trapped there by surface tension. Exercise caution when determining death of the animals. Occasionally, an animal seems dead, but closer observation shows slight movement of an appendage or a periodic spasm of its entire body. For this test, animals exhibiting any movement, when touched with a needle, should be considered alive. To assure accuracy, all 20 test animals must be accounted for.

Evaluation. Determine TL50 values at 48 hours by the interpolation method described in the twelfth edition of "Standard Methods for the Analysis of Water and Wastewaters."

Biodegradability and Oxygen Demand

Since biodegradability or oxygen demand factors have a substantial bearing on the selection of a particular chemical

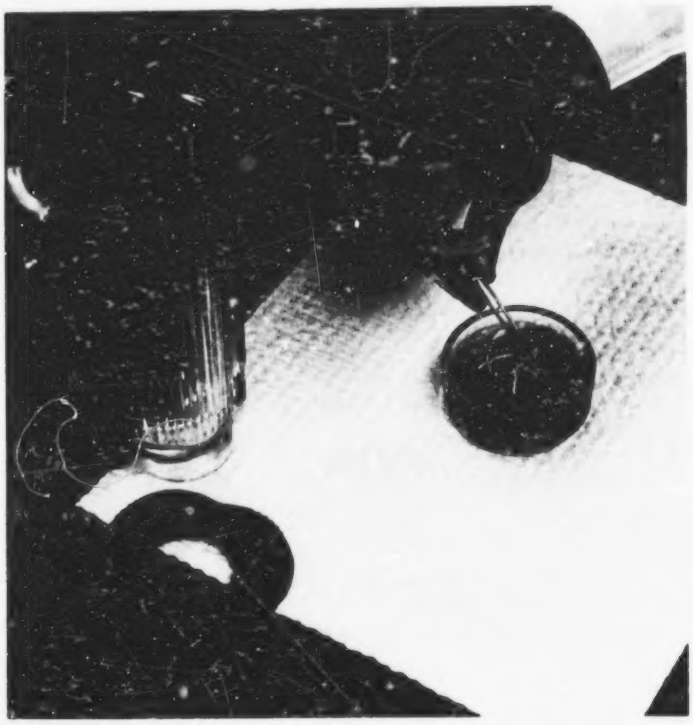

Figure 6. Inoculating twenty Artemia nauplei into the assay dish.

Figure 7. Incubating assay dishes at constant temperature; fluorescent lights under shelf are diffused with white plastic sheets.

material to treat oil floating on water, it is recommended that pertinent data be made available. Such data should consider the chemical material alone and in combination with both fuel and crude oils.

When degradation occurs with the uptake of free oxygen, the common BOD test (as reported in *Standard Methods)* or a manometric test (see *Standard Methods,* 11th edition, p. 393 for details, or Umbreit, W. W., R. H. Burris, and J. F. Stauffer). *Manometric Techniques and Related Methods for the Study of Tissue Metabolism,* (4th ed., Burgess Publishing Company, Minneapolis, 1964, for a general procedural discussion) should be used to determine the extent and rate of oxygen demand. It is recommended for the *Standard Methods* test that at least one blank and three dilutions be used and that the test be conducted for a period of at least twenty (20) days. In cases where the manometric technique is used, the test should be continued until uptake ceases as evidenced by a fluctuation in the sample manometers.

When procedures are available for quantitative analysis of *components of dispersants,* the rate and extent of their biodegradation should be determined. A method similar to those proposed for synthetic detergents may be suitable. For an example, see the "presumptive (shake flask) technique" of the interim procedures recommended by the Soap and Detergent Association for anionic detergents and published in *Soap and Chemical Specialties* (1965)41(4)63.

TABLE 1
REQUIRED EQUIPMENT AND SUPPLIES
FOR BIOASSAYS WITH *ARTEMIA*

Item	Quantity
Laboratory balance, 200 - 0.1 gm*	1 ea
Pipettes, 0.1, 1.0, 5.0, and 10.0 ml*	5 ea
Microliter syringes	2 ea
Weighing papers, glassine*	1 pg
Beakers (Pyrex)* 1 liter	2 ea
Beakers (Pyrex)* 500 ml	2 ea
Beakers (Pyrex)* 200 ml	2 ea
Beakers (Pyrex)* 20 ml	100 ea
Graduated cylinders,* 1 liter	2 ea
Graduated cylinders,* 100 ml	2 ea
Carboy, aspirator outlet, with cover	1 ea
Magnetic stirrer and Teflon-coated stirring bar	1 ea
pH meter or indicators, accurate to 0.1 pH*	1 ea
Carolina culture dishes or equivalent 3½" x 1½" (with petri-dish covers)	100 ea 100 ea
Binocular dissecting microscope*x	1 ea
Beam light source*	1 ea
Chemical spatulas*	10 ea
Blender	1 ea
Air or water temperature control to accomodate dishes (± 1°C) *x	1 ea
Reagents (see text)	—
Silicone rubber tubing	5 ft
Pinch clamp*	1 ea
Long eyedroppers	4 ea
Thermometers (std. immersion type)*	5 ea
Test tube rack*	1 ea
Deep tray of 200 sq. in. surface area (hatching chamber)	1 ea
Syringes	10 ea
Artemia eggs	1 cn (15 oz)
Stop watch*	1 ea
Piston-type Teflon pestle homogenizer - 30 ml	5 ea
Micro cover glass forceps	3 ea
Rubber tubing (1/8" bore, 1/32" wall)	12 ft
Mouthpieces	12 ea
Laboratory cart*	1 ea

* Standard Laboratory Equipment
x Absolute necessity not firmly established

Test Oils

The fuel and crude oils used for tests shall conform to the following specifications:

1. No. 2 fuel oil per ASTM Specification D-396-67
2. No. 6 fuel oil per ASTM Specification D-396-67
3. West Texas crude oil of Permian Basin origin having general characteristics of typical McElroy field crude oil.
4. Venezuelan crude oil having general characteristics of typical Bachaquero field crude oil.

TABLE 2
Typical General Characteristics of Crude Oil

Property	McElroy	Bachaquero
°API	31.5	14.7
Viscosity-SSU	53	3,310
Sulfur - %	2.4	2.6
Asphalt %	18.5	32.8
Naphtha – % to 390°F	25.0	6.0
Gas Oil - % 390 to 620°F	26.0	17.0
Heavy Distillate - % 620 to 760°F	17.5	10.0
Residuum %	29.5	65.0

Test Laboratories

The commercial or university laboratory selected to develop toxicity and biodegradability data shall have suitable equipment, technical expertise and substantial prior experience in aquatic bioassay testing. In the event that more than one laboratory is selected to develop these data, similar test data (e.g., all fish toxicity data) should be developed in a single laboratory. The Federal Water Pollution Control Administration may at its discretion make confirmatory tests of the data supplied.

References

1. "Standard Methods for the Examination of Water and Wastewaters Including Bottom Sediments and Sludges," 12th Edition, American Public Health Assoc., New York (1969).

2. Worlke, Charles E. (1961). Bioassay–the bi-valve larvae tool. Proc. 10th Pacific N.W. Symposium on Water Pollution Control, Portland, Oregon, pp 113-123.

Dispersant Toxicity Test Procedures

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Abstract

The toxicity of chemicals used to disperse oil is considered on the basis of British experience and in relation to effects on fisheries and marine life. It is concluded that although toxic dispersants may be of value in treating oil at sea, they should not be used in large quantities in shallow coastal water, over shellfish beds or fish nursery grounds, or in estuaries. When oil comes ashore the problem should be reduced by mechanical means and chemical methods used only on high-amenity beaches.

Toxicity-testing procedures for dispersants have so far been based upon the determination of LC_{50} *values in static-water aerated tanks at 15°C over a 48-hour period, but a continuous-flow apparatus is being devised. Test animals regularly used are* Pandalus montagui, Crangon crangon, Carcinus maenas *and* Cardium edule, *but the fish* Solea solea *and* Limanda limanda *and the lobster* Homarus gammarus *are now being included.*

A large number of commercially available dispersants have been tested and also some experimental formulations. Some recently-developed materials for use at sea have low toxicities but are of little value for treating oil which has come ashore. Tainting by oil and dispersants may affect fisheries by adding unwanted flavours to fish and shellfish and so affecting marketability over several weeks.

In this paper the investigation of the toxicity of chemicals used to disperse oil at sea and on the shore is discussed in relation to the general problem of the effects on fisheries and marine life of oil and the methods used to deal with oil spills.

In oil spills around Great Britain, the oil involved has usually been either one of the crude oils or a heavy fuel oil. Neither type has been found to be particularly toxic to marine life and it is also a fact that, due to evaporative loss of the lighter fractions, a rapid loss of toxicity takes place during weathering. Consequently, even in the littoral zone, oil alone has done little harm to marine flora and fauna and only sea birds have suffered in this context. Losses to several species of diver and diving ducks have, however, been extensive, and losses of auk species have been specially severe.

There have been no significant spills of refined light oil products such as benzine and kerosene, and we therefore have no experience of the more toxic oil products under British conditions. On the other hand, many of the most effective chemical available to disperse oil and which have proved very useful are highly toxic to marine life.

From the point of view of marine life, there is much to be said for allowing oil on the sea to go ashore and become stranded along the high tide mark, where it can do little harm. However, on a highly populated island such as ours there is usually strong pressure from local authorities and the tourist industry to take immediate effective action to remove the oil.

A number of methods are available which do not involve even mildly toxic chemicals. Mechanical removal is an obvious approach which can be used once the oil has come ashore; in the case of small spills this is often sufficient in itself and it is always a desirable preliminary to chemical treatment, whatever the size of the spill.

Sinking is a non-toxic method which can be used before the oil comes ashore and is useful under the right set of circumstances; however, it should be avoided if an area is regularly fished, because the agglomerated oil is liable to foul fishing gear and thus contaminate catches. Since the

British Isles are surrounded by a heavily-fished continental shelf, there are very few areas near our coast where sinking can be recommended. It is perhaps worth pointing out that, when sinking agents are used, quite apart from the difficulties of spreading which are usually present if a dry finely-divided powder is used, the effectiveness of the method tends to be very variable. If the oil has formed a high-density water-in-oil emulsion, sinking is likely to be successful, since only a very small percentage of sinking agent is required to produce an agglomerate which has a higher specific gravity than sea water. However, the permanent sinking of buoyant, freshly-spilled oils is a much more difficult problem and I know of no case where this has been achieved on a large scale under full sea conditions.

Bearing in mind the facts that mechanical removal is only possible on a large scale once the oil has come ashore and that sinking is not always desirable or even possible, dispersal by chemicals remains an effective treatment which has a place both at sea and ashore.

To the naturalist, the addition of large quantities of toxic chemical to coastal waters is something to be feared, and it is unfortunate that the littoral and sub-littoral fauna which can be so valuable both to the professional biologist and to the amateur naturalist cannot be precisely described in the same monetary terms as can tourist amenities and commercial fisheries.

In assessing the most appropriate method of dealing with oil on the sea arising from a particular spill, it is necessary to take into account the local fisheries and the effects both of oil and of any chemical used to disperse it. In order to make an accurate assessment of the likely effects on marine life, it is therefore essential to have a knowledge of the toxicity to marine animals (and especially commercial species) of the oil dispersants likely to be used.

Oil-dispersing agents can be used in two ways. They can either be sprayed on to floating oil to disperse it at sea, or they can be sprayed on to rocks and beaches to effect cleaning once the oil has come ashore. From the point of view of marine life, these are two separate problems. In the first case, the solvent/emulsifier is rapidly diluted, so that relatively few animals are exposed to the chemical at very high concentration. In addition, the depth of water below the surface layers enables an actively swimming animal to swim clear of the contaminated surface water, assuming, of course, that the animal can detect the toxic agent in time and make an avoidance reaction to it.

When a dispersing agent is used to clean a beach, it is sprayed on undiluted. Although hoses are then played on to the sprayed area to emulsify the oil, the remaining mixture of dispersant, oil and water is still highly concentrated and toxic, and remains so until dispersed by tidal action.

History of Our Test Program

In our earliest experiments in 1962, attempts were made to reproduce in the laboratory both the siutations described above. For our test animals we used a range of molluscan species which are commerically important in Britain. In the first series of experiments, three species of bivalves were dipped into various concentrations of test chemicals for thirty seconds to simulate the spraying of an oiled shore. They were then allowed to drain for two hours, thoroughly washed, and transferred to aerated running sea water for seven days.

It was quite clear that, used in this way, all the solvent/emulsifiers tested were highly toxic to the three species of bivavle used. Over 80 per cent of the winkles, however, were active after seven days. This certainly reflects the efficiency of the seal between the operculum and the shell in this species rather than the physiological resistance of the tissues of *Littorina* to solvent/emulsifiers. It is significant that all the chemicals when applied undiluted caused between 50 and 100 per cent of the winkles to become moribund and extended out of their shells for two or three days before recovery. It is probable that under natural conditions wave action and predators would kill these animals before they had time to recover.

The second series of experiments was designed to assess the toxicity of the oil-spill removers to shellfish if used close to shellfish grounds. Suspensions of the test chemicals at 10, 32, 100 and 320 parts per million were made up in sea water and groups of twenty to twenty-five flat oysters *(Ostrea edulis)*, Portuguese oysters *(Crassostrea angulata)*, mussels *(Mytilus edulis)*, and cockles *(Cardium edule)* were placed for twenty-four hours in aquaria containing these suspensions.

The water was not running but the tanks were well aerated. After twenty-four hours the animals were transferred to clean, running sea water and observed for seven days. It was found that the greatest mortalities were among the cockles, 50 per cent of these being killed by concentrations of "Polyclens" between 32 and 100 parts per million and of "Slix" between 10 and 32 parts per million. Only Portuguese oysters were completely resistant to 320 parts per million of "Polyclens" for twenty-four hours.

The fact that some flat oysters survived in a wide range of concentrations of the chemicals, and that no deaths occurred among the Portuguese oysters, suggests that the oysters, and perhaps also the mussels, were resisting the toxic substances by closing their shells and remaining closed for all or part of the twenty-four hours during which they were exposed to the chemicals. The greater susceptibility of the cockles and the clearer mortality picture given by them were due to the fact that cockles are unable to close their shells as completely as the other bivavles used, and therefore were always susceptible to some degree of penetration of the chemicals to their soft parts.

The experiments described above were designed to enable us to assess the risk to shellfish beds liable to damage during oil-cleansing operations in the vicinity. It was concluded at that time that the use of any solvent/emulsifier, capable of effectively cleaning a shore, in beach-cleansing operations would cause severe mortality to littoral and immediately sub-littoral fauna; no further tests were carried out to compare the toxicity of solvent/emulsifiers used in this way since, whatever product was used, considerable biological damage would be certain. At the time of writing (October 1969) an efficient beach cleaner which is also of low toxicity has yet to come on to the market.

Based on the results reported above, it was decided to continue work on testing the acute toxicity of oil-spill removers as used at sea. This work began in 1965, when Dr. Portmann of our department[1] developed a forty-eight hour static test which was designed to test the acute toxicity to marine animals of a wide range of pollutants, including oil-spill removers. He decided that, bearing in mind the fact that solvent/emulsifiers are normally used for short periods and not discharged continuously, a forty-eight hour static test would be a realistic method for comparing the toxicity of oil-spill removers.

The animals were exposed to a range of pollutant concentrations for a period of forty-eight hours. The tanks were examined at intervals throughout the course of the experiments and animals which had died were removed, the total number of dead being recorded. The results were expressed in terms of a 48-hour LC_{50}, this being the concentration of pollutant required to kill 50 per cent of the test population of twenty to thirty animals. The LC_{50} is analogous with the term TL_{50}, which is used extensively in the United States, though the latter refers to a ninety-six hour test.

Preliminary experiments with other toxins established the fact that temperature markedly affected the resistance of the animals. Consequently all our tests were run at the standard temperature of 15°C, which is equivalent to British coastal water temperatures in summer. The degree of starvation was also found to affect the results, and the use of animals which had been held in the laboratory aquarium for more than a few days was avoided.

Twelve different, commercially available solvent/emulsifiers were used in the first comprehensive series of tests.[2] This work was carried out with four species: two shrimps *(Pandalus montagui* and *Crangon crangon)*, the shore crab *(Carcinus maenas)* and the cockle *(Cardium edule)*. The results showed that, although all the products were markedly toxic, there were nevertheless clear differences both between products and between species.

A number of factors suggested that the solvent fraction was the major toxic component of many of the dispersants, and it was already known from Portmann's earlier work in 1965 that surfactants themselves are frequently not lethal to marine animals under identical experimental conditions at concentrations as high as 100 parts per million. It was also found that comparatively few animals were dying on the second day of the solvent/emulsifier experiments, suggesting that the more toxic fraction was being lost.

In order to investigate this effect, we carried out a series of experiments with sea-water solution containing 50 parts per million of B.P. 1002 (24 hour LC_{50} = 5 p.p.m.) and aged for various times. In these tests, samples of ten flatfish *(Solea solea)* were exposed for twenty-four hours to the variously aged solutions. It was found that although all ten fish died in the fresh solution, there was a clear diminution in the toxicity of those solutions which had undergone aging, and indeed that which had been aged for seventy-two hours did not cause the death of any fish. Since the surfactant is virtually non-volatile and only slowly biodegradable, the observed decrease in toxicity could only be attributed to loss of the solvent fraction by evaporation.

Thus the LC_{50} of a solvent/emulsifier as determined by the forty-eight hour test is always a minimum value. However, because a loss of toxicity by evaporation is bound to occur in the field just as it does in the laboratory, we consider that the forty-eight hour static test is a realistic one.

Of course, under field conditions, there will always be wide variations both in the time of exposure and in the concentration of the dispersant. In order to study this further, animals were exposed to a range of concentrations for various periods up to eight hours. After this, they were transferred to tanks of clean, running sea water for twenty-four hours, and the dead animals were then counted.

It was found that there was close agreement between the eight-hour and 48-hour LC_{50} of the substance tested. However, the lethal threshold concentrations were reached rather more rapidly with shrimps than with cockles, and this may be due to the fact that cockles are able to reduce the flow of water over their soft parts by partially closing their shells. When these experiments were repeated with two species of teleost fish, the sole *(Solea solea)* and the dab *(Limanda limanda)*, and lobsters *(Homarus gammarus)*, very similar curves were obtained.

Discussion

It is of interest to note that during the course of these experiments it was frequently found that moribund animals would apparently recover in the clean water. This is certainly an effect which requires further investigation, since it is highly unlikely that the apparently recovered animals were, in fact, undamaged. For instance, Wilson[3] found that larvae of the phychaete worm *Sabellaria spinulosa*, which had apparently recovered from exposure to the solvent/emulsifier B.P. 1002, died some weeks later, in contrast to controls which remained active and normal. Situations of this kind do emphasize the need for more fundamental work on the mechanisms by which dispersants exert their toxic effects. There is scope here for work by the physiologist and the electron microscopist to supplement the relatively large quantity of ecological data which is now available.

Portmann's program of dispersant toxicity testing had not long been started when the *Torrey Canyon* disaster occurred, on March 18, 1967. As is now well known, an approximate total of 100,000 tons of Kuwait crude oil was spilled on to the sea as a result of this wreck. At that time, in addition to Portmann's program of work on adult commercial species, Dr. J. H. Blaxter (University of Aberdeen) and Dr. J. E. Shelbourne of the Ministry's staff at Port Erin, Isle of Man, and scientists at the Marine Biological Association Laboratory, Plymouth, began urgent dispersant toxicity-testing programs of their own.

Blaxter and Shelbourne worked on the larvae of sole and plaice, while the Plymouth scientists and university workers concentrated on non-commercial species from a wide range of animal groups, zooplankton and phytoplankton. A summary of the comprehensive program of experiments carried out at this time is given by Smith.[4] As in the results of Portmann and Connor,[1] the solvent fraction of the dispersants was found to be considerably more toxic than either the stabilizer or the surfactant.

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[1] Superior numbers refer to literature references at conclusion of text.

The work on zooplankton showed that small marine animals were more susceptible to damage by oil dispersants than larger forms. Similar results were obtained by Portmann and Connor[1] when the susceptibilities of adult and larval shore crabs *(Carcinus maenas)* and brown shrimps *(Crangon crangon)* were compared. A particular instance of this size effect was recorded by Sparrow and quoted by Smith;[4] this worker showed that the resistance of *Calanus finmarchicus* to dispersants was much greater than that of the smaller copepod *Acartia clausi.* Since it is likely that solvent/emulsifiers exert some of their toxic effects at exposed surfaces, it is not unexpected that animals with a high surface/volume ratio are most susceptible to these substances.

The interesting experiments by Wilson[3] on *Sabellaria* larvae have already been mentioned. The results obtained are a particular instance of the special susceptibility of larvae. Although some of this greater susceptibility could be explained by suface/volume considerations, it does seem that developing animals are especially susceptible to concentrations of substances which, though not immediately lethal, cause ultimate death by interfering with developmental processes. Evidence that developmental processes were being disrupted was also found by Corner *et al.*[5] in their study of the effect of solvent/emulsifiers on the larvae and adults of the barnacle, *Elminius modestus.*

Results obtained by the Plymouth group of workers for adult sub-littoral species fell within the same range as Portmann and Connor's[1] results for commercial shellfish. Bivalve molluscs were found to be particularly sensitive, especially the razor-shell *(Ensis siliqua),* and the most resistant species tested were the hermit crab *(Diogenes pugilator)* and the common starfish *(Asterias rubens).*

Both Portmann and Connor[1] and the Plymouth scientists carried out tests in which crude oil was mixed with a solvent/emulsifier; the results of both groups of workers indicated that mixtures of this kind were less toxic than solvent/emulsifiers alone. Presumably interaction between the oil and the dispersant reduces the toxicity of the latter by removing some of it from free solution.

Since the *Torrey Canyon* disaster a large number of oil dispersants have been tested using the 48-hour test and it is very gratifying to be able to record the low toxicities of some of the recently developed dispersants (Correxit and Dispersol) which do not contain aromatic solvents, though they are of little value on oil which has come ashore.

The 48-hour static test, for all its limitations, has proved to be a most useful research tool which has enabled us to make a rapid comparison of the acute toxicities of a wide range of oil dispersants. However, because it is such a short test and takes no account of long-term or sub-lethal effects, it does not define safe levels. Due allowance must be made for this when the results of short-term toxicity tests are used in assessing the likely effect on fisheries of particular dispersants in the field.

At the present time we are developing a continuous-flow toxicity-testing apparatus which will enable us to maintain toxic concentrations at a fixed level and also to look at the effects of long-term exposure to low concentrations of dispersants. Although this is not very likely to occur in the field at any single area of oil spillage, it is certainly likely near oil terminals and bunkering stations where small spills are a relatively frequent event. In our apparatus, toxin is metered into a previsely controlled flow of sea water which is led via a mixing chamber into the test tank.

The reliability of the apparatus depends on good flow control. In our design we achieve this with variable height siphons, thus eliminating all taps and constructions which are liable to accumulate any fine solid material that passes the filters. We expect to be using this technique on a routine basis from the beginning of 1970.

Sub-lethal effects. At the present time very little is known about the sub-lethal effects of oil dispersants and to what extent these are reversible. One would expect tissue damage to appear first of all at exposed surfaces such as gills, chemosensory areas, etc. A careful study of their fine structure before and after exposure to dispersants and after a "recovery" period is likely to be rewarding. We are planning to carry out some behavioural observations along these lines, in an attempt to assess the consequences of sub-lethal damage to chemosensory systems in fish and shellfish.

An important factor in any form of pollution is the extent to which it can be detected by the sensory systems of the animals involved; if it can be detected in time, it is possible for mobile species to swim away from it and thus avoid damage. In the case of oil dispersants we have evidence, from experiments with a Sprague-type trough,[6] that the shrimp, *Crangon crangon,* can detect and avoid solvent/emulsifiers at a dilution over one hundred times greater than their 48-hour LC_{50}. However, in the case of dispersants which do not use an aromatic solvent this detection level is only a seventh to a tenth of the 48-hour LC_{50}.

Tainting. Although the question of toxic effects must always be a very important factor to consider in assessing the effect on fisheries of particular instances of pollution by oil and dispersants, it has been our experience that in many cases greater economic harm is caused by tainting than by toxic effects.

Tainting by oil alone is common in the case of littoral molluscs such as mussels, where oil settles on the shell and taints the flesh during cooking. During stormy weather, oil on the sea may become emulsified and the small oil globules formed can be ingested by filter-feeding shellfish, causing tainting. We have also had reports of fish, caught near a bunkering station, which, although apparently healthy, were rendered quite inedible by the strong flavour of mineral oil which permeated the flesh; in this case, violatile fractions in solution in the harbor water were almost certainly the cause.

The use of dispersants can also lead to tainting both by globules of dispersed oil and by the dispersant itself. Isolated cases of tainted fish (plaice and sea-trout) were recorded after the *Torrey Canyon* spill.[7] In the case of lobsters there was evidence of tainting in both free-living animals and those held in store pots, and due to fear of affecting the market, the fish merchants would not accept lobsters from one part of the coast for three weeks. The paraffin-like taste of the affected animals suggested that the aromatic solvent of the dispersant was the most likely cause of the tainting.

Conclusion

Although work remains to be done on the mechanisms of toxicity and the sub-lethal effects of oil dispersants, enough information is available to enable recommendations to be made on the type of treatment that should be stipulated to minimize harm to fisheries and marine life in any particular spill.

In cases when it is inevitable that the oil will come ashore it can be helpful to use chemical treatment to disperse it in deep water, where cheap though toxic solvent/emulsifiers can be used with little risk to marine life. In shallow water, a less toxic, though usually more expensive, dispersant may be justified. Once the oil has come ashore the preferred method depends on local conditions and the purposes for which the coastal waters and beaches are used.

From the fisheries point of view, toxic solvent/emulsifiers should certainly not be used in large quantities in shallow coastal areas and especially over fish nursery grounds or near shellfish beds. Similarly, the use of solvent/emulsifiers would not be recommended in or near the estuaries of salmon or sea-trout rivers when these fish are migrating. Ideally, when oil does come ashore mechanical methods of removing it should be used as far as possible, and chemical methods should be used only in cleaning up operations where a beach has high amenity value.

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Laboratory Evaluation Of Chemical Oil Dispersants

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Abstract

This paper describes some of the methods which can be used to evaluate chemical oil dispersants in order to obtain some preliminary data related to their effectiveness as dispersants and problems that may result from their use. Most of the techniques are quite simple and can be done fairly rapidly in the laboratory. Some of these were borrowed from the standard procedures employed in water and wastewater treatment practices and include jar tests, bioassays, oxygen uptake measurements and threshold odor determinations.

Data derived from these tests may be of some value in situations where a selection of a suitable dispersant must be made on the basis of only limited knowledge and experience.

Since the disaster of the ill-fated *Torrey Canyon* in 1967, many chemicals and materials have been developed and introduced commercially to combat floating oil slicks resulting from accidental oil spills and to control subsequent oil pollution problems.[1,2] Several of these products are chemical oil dispersants which are also referred to as degreasers, detergents and emulsifiers. When applied to oil-water mixtures, they help to disperse or solubilize the oil into small globules and form emulsions. The oil dissipates more readily in water and becomes less objectionable in appearance. Many of these chemicals are well-publicized as being non-toxic to aquatic life and readily biodegradable.

Experiences after the *Torrey Canyon* incident and at Santa Barbara have led to the conclusion that some of these chemical oil dispersants employed in removing and dispersing the oil in the affected areas were far more deadly and far more damaging to marine life and ecology than the oil itself.[3] In addition, recent experiences at Santa Barbara have shown that they introduced more problems. When applied to beaches, they caused the oil to penetrate more deeply into the beach sand making it more vulnerable to erosion by tidal and wave action.[4]

The Ontario Water Resources Commission, a regulatory body organized in 1956 by the Ontario Government, is charged with the responsibility of safeguarding and protecting the water resources in the province of Ontario through control over all sources of pollution. The Commission has been concerned with the problems of dealing with oil pollution and its cleanup whether it has been caused from waste discharges or accidental oil spills.

One area of concern has been the limited information available on the use of these chemicals and their possible deleterious effects on the water quality of fresh water with respect to tastes and odors and toxic properties on the aquatic life. For this reason, it was decided to set up a test program whereby these oil dispersants could be evaluated quickly without any elaborate procedures.

It is the purpose of this paper to outline some of the methods which were used to evaluate some of the chemical oil dispersants in the laboratory, to compile some pertinent data that might be useful in selecting a suitable chemical for oil cleanup, and to assess some of the adverse effects that may result from their use.

Chemical Characteristics Of Oil Dispersants

A cursory review of the literature has revealed that many of these chemical oil dispersants are essentially a

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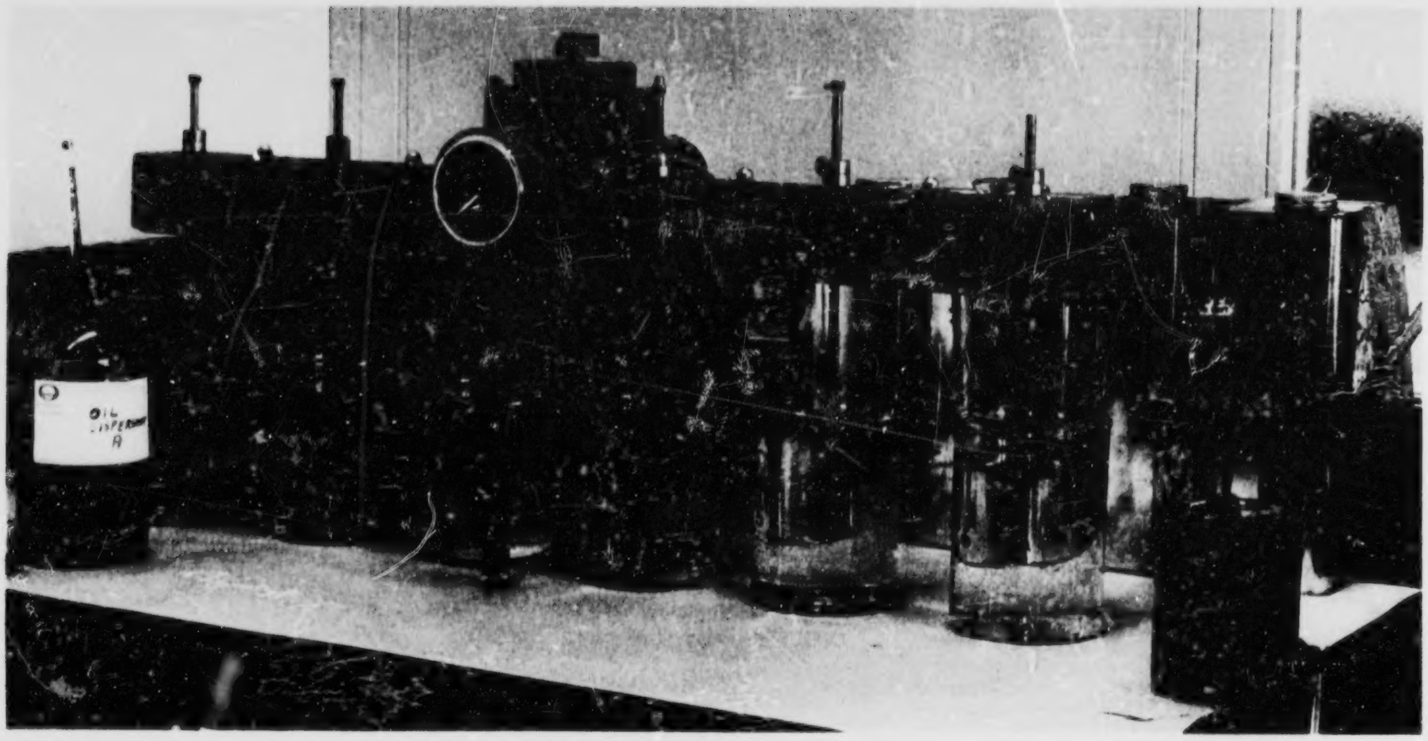

Figure 1. Tests with a multiple stirrer to obtain preliminary data.

formulated mixture of several compounds consisting of a non-ionic surface-active agent (surfactant), an organic solvent and a stabilizer.[5] The non-ionic surfactant may consist of polyethanoxy compounds of polyglycols. These are widely used in the preparation of cleaning agents and detergents formulated for cleaning and removing oily materials and other petroleum derivatives. The solvents usually consist of high aromatic hydrocarbons such as kerosene which allow the surfactant to mix with the oil and form an emulsion with water. Stabilizers are added in the formulation to achieve stable emulsion and this, in turn, enhances the dispersion of the oil in water.[5,6]

The function of the chemical oil dispersant is not to destroy or remove the oil. Its primary purpose is to increase the surface area of an oil slick by breaking it up into small globules. This action helps to disperse the tiny globules throughout the large volume of water so that they become more susceptible to biological degradation. The oil slick dissipates over a wide area and becomes less objectionable in appearance.

Test Procedures

General. Several commercially available chemical oil dispersants were evaluated in the laboratory with tests on samples of Canadian crude oils and fuel oils consisting of Bunker C and diesel oil. The crude oils tested were obtained from the local refineries and included those from Alberta, Saskatchewan and Ontario.

The tests were conducted by utilizing simple laboratory equipment for the primary purpose of obtaining some preliminary data from which a selection of a suitable chemical could be made with a minimum time to handle oil spills in a particular situation. It was also felt necessary to consider some of the detrimental effects and other unforeseen problems that may arise from the use of these chemicals in fresh waters, especially if they were applied in excess quantities.

Essentially, these tests were developed to utilize some of the standard laboratory procedures and readily available equipment to evaluate these chemicals and to compile some pertinent data with regards to their:

1. Effectiveness as oil dispersants,
2. Biological treatability,
3. Toxic effects on fresh water fishes and
4. Effects on the palatability of water.

Tests for Effectiveness. Two methods were used to evaluate the effectiveness of these chemicals as oil dispersants. They both involved the application of oil dispersants on a patch of oil floating on water and then agitating the water by means of a mechanical device.

The first method was used to determine the approximate dosage of chemical that was needed to disperse a given volume of oil floating on water. It involved the use of a multiple stirrer (Figure 1), an apparatus employed in waterworks plants to determine coagulant dosages. Here, a sample of oil, usually 10 ml, was placed in a 1-litre beaker of tap water and then treated with the undiluted dispersant. The latter was applied carefully onto the surface of the floating oil slick by means of a small pipette, one drop (0.1 to 0.5 ml) at a time. After each drop, the entire contents of the beaker was stirred vigorously for a few minutes and then stopped. A few minutes later, another drop of chemical was added on the oil slick and then stirred. This process was repeated until all of the oil had been dispersed completely or at least when a predetermined dosage of chemical had been added.

In the second method, an attempt was made to simulate the conditions likely to be encountered on open waters which are subjected to wave actions. A small volume of oil (5 to 10 ml) was spilled on the surface of the water in a shallow rectangular pan placed on a mechanical shaking device—the Dubnoff Metabolic Shaker (Figure 2). The latter operates in circular motion moving back and forth in a horizontal plane. Its speed could be easily regulated to provide gentle or vigorous movements in the water, similar in effect to the natural wave actions produced on lakes or other bodies of open water. The chemical was applied as a fine spray on the oil slick while it was being tossed around on water by the shaker. Spraying of the dispersant was achieved by means of a spraying device fitted on an aerosol bomb containing a pressurized propellant. Wherever applicable, the solution of dispersant was made up in accordance with the manufacturers' instructions. Spraying was continued until nearly all of the oil slick was dispersed.

Biological Treatability. The biological treatability of the oil dispersants was determined by techniques and equipment similar to those described by Lamb and his associates.[7] This involved the use of a respiration cell and a membrane-covered oxygen electrode to measure activity and oxygen utilization rates of an endogenous sludge that had been fed with varying amounts of oil dispersants.

For testing purposes, a sample of mixed liquor sludge obtained from an activated sludge treatment plant was brought to an endogenous state by aeration without any feed for a period of 12 to 24 hours before the test.

Toxicity Studies. The toxic effects of these oil dispersants were determined by the routine bioassay methods[8] employing *Pimphales promelas* as test animals. These methods have also been developed as "Interim Toxicity Procedures" by the Federal Water Pollution Control Administration[9] for evaluating the acute toxicity of materials to be used for the control of oil pollution.

Threshold Odor Tests. Standard threshold odor tests at 140°F were performed on a series of tap water samples contaminated with trace quantities of oil dispersant. The test samples were made up from odor-free water containing 1 ppm or 10 ppm oil dispersant, depending upon the intensity of the odor emitted by sample. Similar tests were also conducted on another series of samples containing oil dispersants but treated with marginal amounts of chlorine solution (sodium hypochlorite).

Discussion

Earlier studies by the author[11] have shown that several of the chemical dispersants had varying degrees of dispersing power with different samples of crude oil tested. Some were found to be more effective than others in the treatment of one particular sample of crude, and less effective on others, particularly those with higher sulphur content and heavier oils.

The action of the dispersant could be further complicated by the weathering phenomenon whereby the crude oil may undergo major physical or chemical changes,

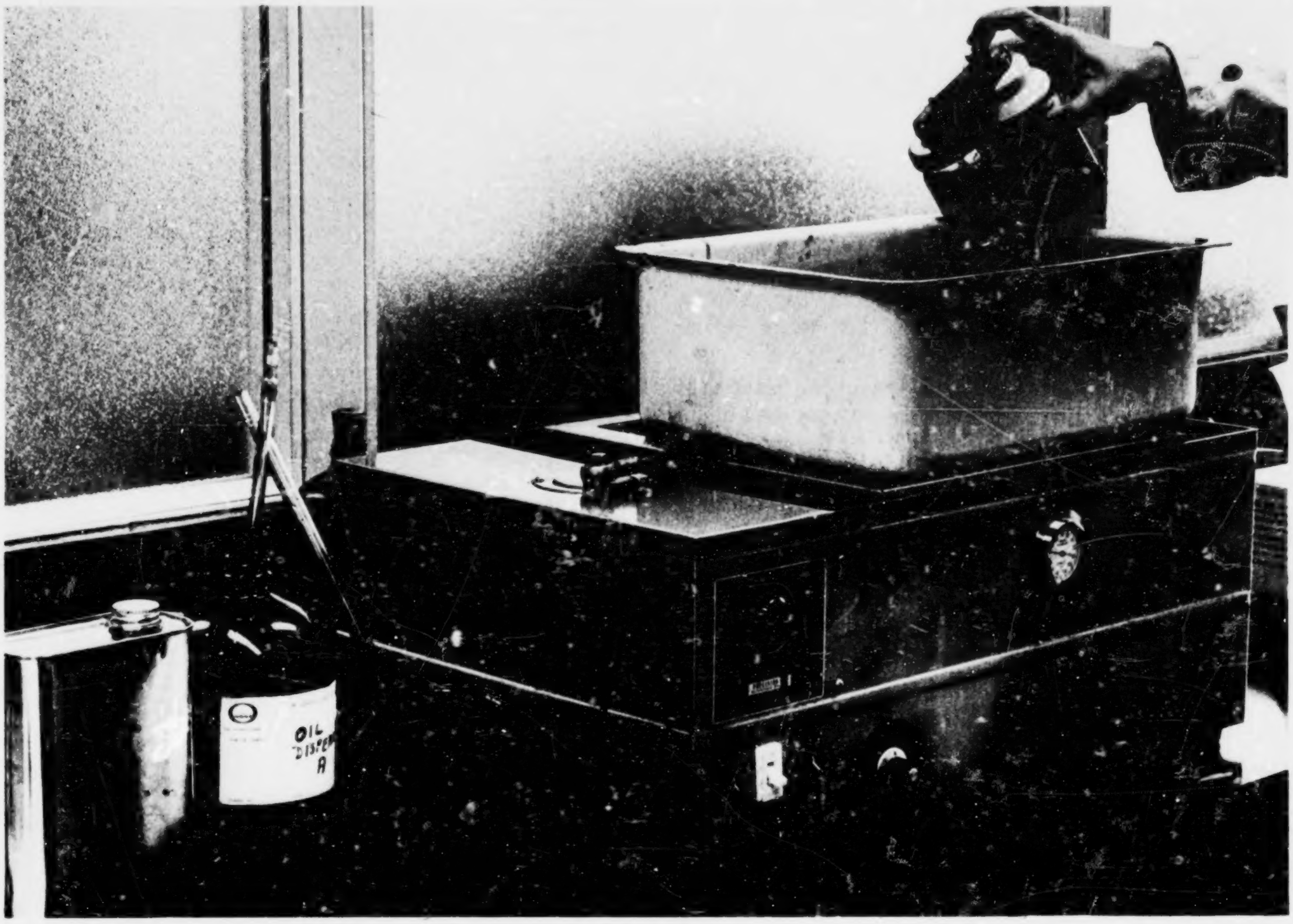

Figure 2. Equipment used for applying oil dispersants under test conditions.

especially when it is subjected to variable environmental conditions. Oil spills on open waters are exposed to natural elements such as the sun and the wind. The character of the oil may change drastically due to loss of its volatile fraction by evaporation, oxidation and biodegradation of some of its other components. Finding a suitable chemical dispersant to cope with oil spills under these conditions would undoubtedly be a difficult task.

Tests for Effectiveness. The results obtained from tests with the multiple stirrer will give some preliminary indication of how effectively a particular sample of crude or fuel oil will respond to the treatment with the dispersant. Also, it is possible to determine the approximate dosage required to disperse and emulsify the oil.

Although the methods are somewhat crude, they offer several advantages:

1. Preliminary data concerning dosages and relative effectiveness of the dispersant can be obtained very quickly.
2. Behavior of the oil treated with the dispersant can be observed and studied very easily, for example, stability of dispersant-oil emulsions.
3. Least effective dispersants can be eliminated at once.
4. Comparative tests can be performed simultaneously on several samples of dispersants.
5. Tests are very simple and do not require sophisticated equipment or methods.
6. Tests can be conducted under controlled environmental conditons, notably temperatures and water quality.

These tests also have some limitations and therefore the data obtained must be treated accordingly. Some of these are as follows:

1. A good portion of the dispersant may not come into contact with the floating oil during the test but instead, it may dissolve into the water before reacting completely with the oil.
2. It was difficult to evaluate the dispersing qualities of some dispersants which performed very well under constant agitation, but quickly re-formed into a slick the moment the agitation ceased.
3. A large portion of oil will adhere to the test equipment and thus reducing significantly the amount of test sample available for treatment with the dispersant.
4. Test samples are likely to be subjected to a much greater amount of agitation than that under actual field applications.

Biological Treatability. The purpose of the biological treatability test is to evaluate the effect of chemicals or any toxic materials on biological treatment systems. This is a technique which is frequently employed in sewage treatment plants to assess the treatability of industrial wastes by biological methods. It involves the determination of microbial activity in an activated sludge system by measuring its oxygen utilization rate or the rate at which the oxygen is being depleted.

When a sample of an endogenous sludge is fed with the chemical, there will be a pattern of oxygen depletion rate governed by the activity of microorganisms in utilizing this material. Some of the typical curves obtained by plotting the test data are illustrated in Figure 3.

Curve I (dotted line) represents a pattern of oxygen utilization rate exhibited by an endogenous sludge before being fed. If the material fed to the sludge is biodegradable, its compatibility or consumption is indicated by an increased activity by the organisms and also reflected by an increase in the respiration rate or the depletion rate of oxygen. This is represented by Curve II and it has a greater slope than of Curve I.

Curve III illustrates the case when the material added has no effect on the microorganisms and usually it has the same slope as that of Curve I representing the endogenous state.

If the material feed is increased and becomes toxic or shows inhibitory effects on the activity of the organisms, the respiration rate will decrease as illustrated by Curve IV.

The data derived from these tests may be useful in predicting the effect of certain dispersants on sewage treatment processes, particularly in cases where significant quantities of oily wastes and petroleum products are discharged into municipal sewers. The application of excess amounts of dispersant may have a toxic effect and upset the activated sludge process at the sewage treatment plant. Therefore, they may be of special interest to operators of sewage plants where oily wastes are liable to cause some operating difficulties.

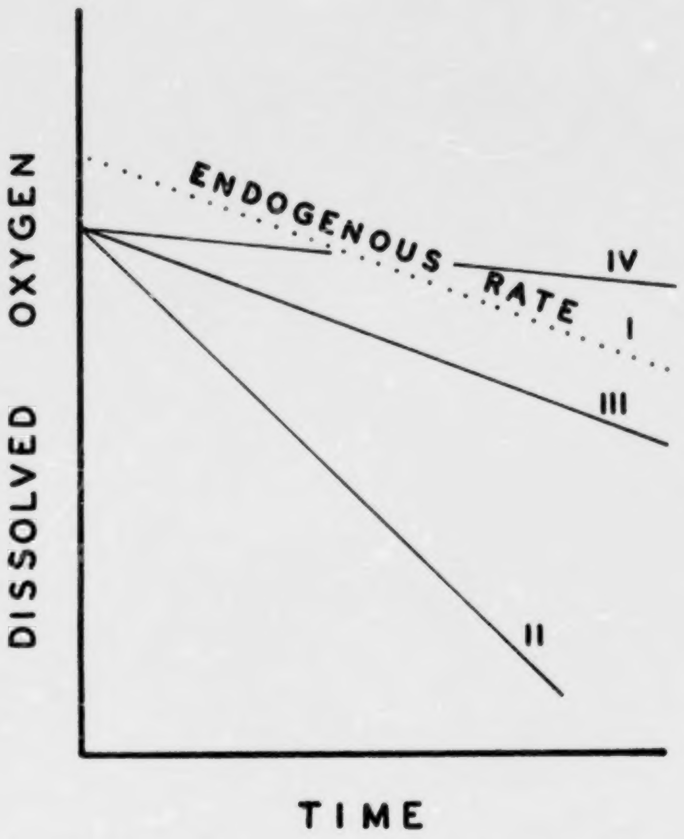

Figure 3. Curves showing oxygen utilization rates of an endogenous sludge fed with varying amounts of an oil dispersant.

The data may be of some value in determining the biodegradability or the fate of some of these dispersants in natural waters. In other words, if any chemical were found to be highly toxic to the microorganisms at very low levels of concentration, then it could have long term effects on the environment.

Odor Tests. Many of the chemical dispersants are mixtures containing dispersing agents dissolved in either hydrocarbon solvent or water. The solvent may consist of highly odorous materials. If present as a contaminant in public water supplies, even in trace quantities, there is a possibility that the taste and odor quality of the water may be adversely affected. In some cases, this problem may be aggravated by chlorination practice. Chlorine, a disinfectant employed in the purification process of water, may react with the dispersant to form a by-product which imparts very strong flavors to the water.

Data from the odor tests may be valuable in the selection of an appropriate chemical for dispersing oil slicks in waters where municipal water supplies may be contaminated.

Toxicity. There are a large number of chemicals available on the market for the purpose of removing oil slicks from water. Many of these have been well-publicized as being non-toxic and harmless for use in water. However, several studies[3,11,12] have demonstrated that many of these exhibited varying degrees of toxicity to various forms of aquatic life.

Although standard procedures have not yet been established to evaluate a precise concentration for the acute toxicity of these chemicals, nonetheless the results of the bioassay tests will provide some preliminary information which may be of an important consideration in the selection of a proper dispersing agent.

Summary

A description is given of some preliminary tests that may be performed to evaluate chemical oil dispersants in the laboratory for their efficiency in cleaning up and controlling oil pollution and to assess some of the adverse effects resulting from their use. Most of the techniques were borrowed from the standard procedures utilized in the field of water and wastewater treatment such as jar tests, toxicity studies, oxygen uptake measurements, and threshold odor determinations.

Until some standard procedures have been developed for evaluating oil dispersants, the data derived from the above tests will be of some value in situations where limited knowledge is available on a specific chemical and a quick decision must be made to choose a suitable chemical to remove an oil slick from the water.

The tests are simple and can be done fairly quickly. No elaborate equipment is required. The test data can be used as a guide to determine the effectiveness of an oil dispersant in a given situation, to estimate an approximate dosage, and to predict some of the possible difficulties that may result from indiscriminate use.

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Evaluation Of The Effectiveness Of Oil-Dispersing Chemicals

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Abstract

A procedure for evaluating the effectiveness of oil-dispersing chemicals has been developed. Using the apparatus originally designed for the Navy specification for solvent-emulsifiers, test conditions were adapted to correspond more closely to typical environmental conditions. Test conditions having the greatest effect on dispersant performance included: type of oil, composition of salt water solution, degree of agitation of chemical/oil mixture, and the degree of contact between chemical and oil prior to agitation. Results from this modified procedure, the Simulated Environmental Tank (SET) Test, correspond well with results from simple field tests. Field tests have limited precision and reproducibility. This lack of a reliable index of field performance with which to compare laboratory results hinders refinement of standard test procedures. The SET Test, which produces results corresponding favorably with field performance, to the extent field performance can be determined, and which simulates typical environmental conditions, is proposed as a meaningful interim solution to this problem of dispersant evaluation.

The application of massive quantities of "detergents" during the *Torrey Canyon* incident provoked a controversy over the use of oil-dispersing chemicals which persists today.[1] The immediate reaction to the *Torrey Canyon* affair was, of course, primarily in response to the toxicity to marine life of most of the dispersants then available.[2] This concern for environmental effects stimulated a reappraisal of the more fundamental problem of the desirability of dispersion as a basic approach to the handling of oil spills. For instance, how toxic is oil itself, when dispersed, to marine organisms? What is the ultimate fate of oil in the marine environment? Very likely the answer to these and similar questions will determine the future role of dispersion as a method for the control of oil pollution.

But effects on the environment are not the only considerations in the use of dispersants. Assume, for instance, that large quantities of dispersed oil could be tolerated by the environment, and that relatively innocuous dispersants were to be developed, as indeed they already may have been. The basic question still remains, "how well will they work?" Obviously, it would be futile to develop a dispersant ten times less toxic than those now available if ten times as much must be used to disperse a given quantity of oil. Performance also must be considered, and for this some means of determining the effectiveness of dispersants is required.

At first this would seem to be a rather straight forward problem. A basic definition of dispersant performance might be expected from reports of the use of dispersants during actual spills. However, quick search of the literature immediately dispells this hope. Eyewitness accounts present a diverse range of opinions on the effectiveness of chemical dispersion—usually subjective and without documentation, and often seeming to reflect the particular interests of the observer.[2-10] Even with cases of reportedly effective dispersion, the nagging question always arises, "What would have happened to the oil had dispersants *not* been used?" The sea possesses its own poorly understood, but impressive, powers of dispersion.[6] Several times in the area of New York Harbor we have witnessed the essentially complete disappearance of over a thousand barrels of untreated heavy oils within the period of several hours. These observations may be the results of processes unique to that rather polluted estuary but they tend to support the conclusion that, under certain conditions, oil may disperse fairly rapidly without any help from man.

In view of the complexity of the process of emulsification, and the diverse number of environmental factors influencing the dispersion of oil from the surface of water, the disparity of reports on field performance of dispersants

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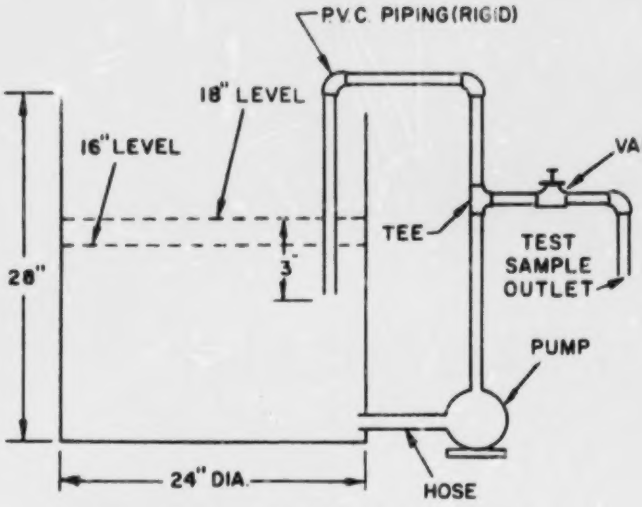


Figure 1. Schematic diagram of test apparatus.

is understandable. Similarly, it is easy to see why controlled field tests with dispersants have generally resulted at best in a rather gross rating of effectiveness.[11-13]

How then is the effectiveness of dispersants to be determined? For routine comparison of the hundred or more products now available, it is desirable to have the reproducibility, precision and economy of a laboratory procedure. A number of simple laboratory tests have been developed for this purpose,[14-16] but most of these can be challenged on the ground that their results haven't been shown to correspond to field results. A slight change in mixing energy or method of adding dispersant can markedly influence test results. Without a measure of field performance as a yardstick for comparison, the relevance of their results remains in question.

In an attempt to relieve this dilemma without awaiting major advances in the state-of-the-art, we began a search for a meaningful standard procedure for evaluating dispersant effectiveness which would be reproducible from day to day and from laboratory to laboratory. It became immediately obvious that no single set of test conditions would account for all the variables involved in dispersion. Some sort of compromise would be necessary to develop a standard procedure.

The Navy appeared to have adopted a rational approach to this problem several years ago with their specification for solvent-emulsifiers, the so-called Navy Tank Test,[17] and we took this test as our starting point. This test combines the advantages of a laboratory procedure with an attempt to *simulate* environmental factors. Figure 1 illustrates the apparatus used. It consists of a cylindrical tank 28 inches high and 24 inches in diameter, with a system for recirculating the tank contents from the bottom to just below the surface of the water. This simulates the subsurface mixing of natural waters. In the test 100 ml of oil is poured onto the surface of the water, followed by 100 ml of chemical. After one minute this oil/chemical mixture is agitated by hosing with a stream of water under standard conditions. The tank contents are allowed to recirculate for ten minutes and a sample of the water phase withdrawn. This same is extracted with an organic solvent and the oil measured in a spectrophotometer. Results are expressed as per cent of the original 100 ml of oil dispersed–that is, recovered from the underlying water.

Results

For examination of this procedure, we selected four test oils to cover the range of properties likely to be encountered–(Table 1) a light, Louisiana crude; a heavy, high asphaltic, Venezuelan crude; a refined product, No. 2 fuel oil; and a residual fuel oil, No. 6 fuel oil or Bunker C.

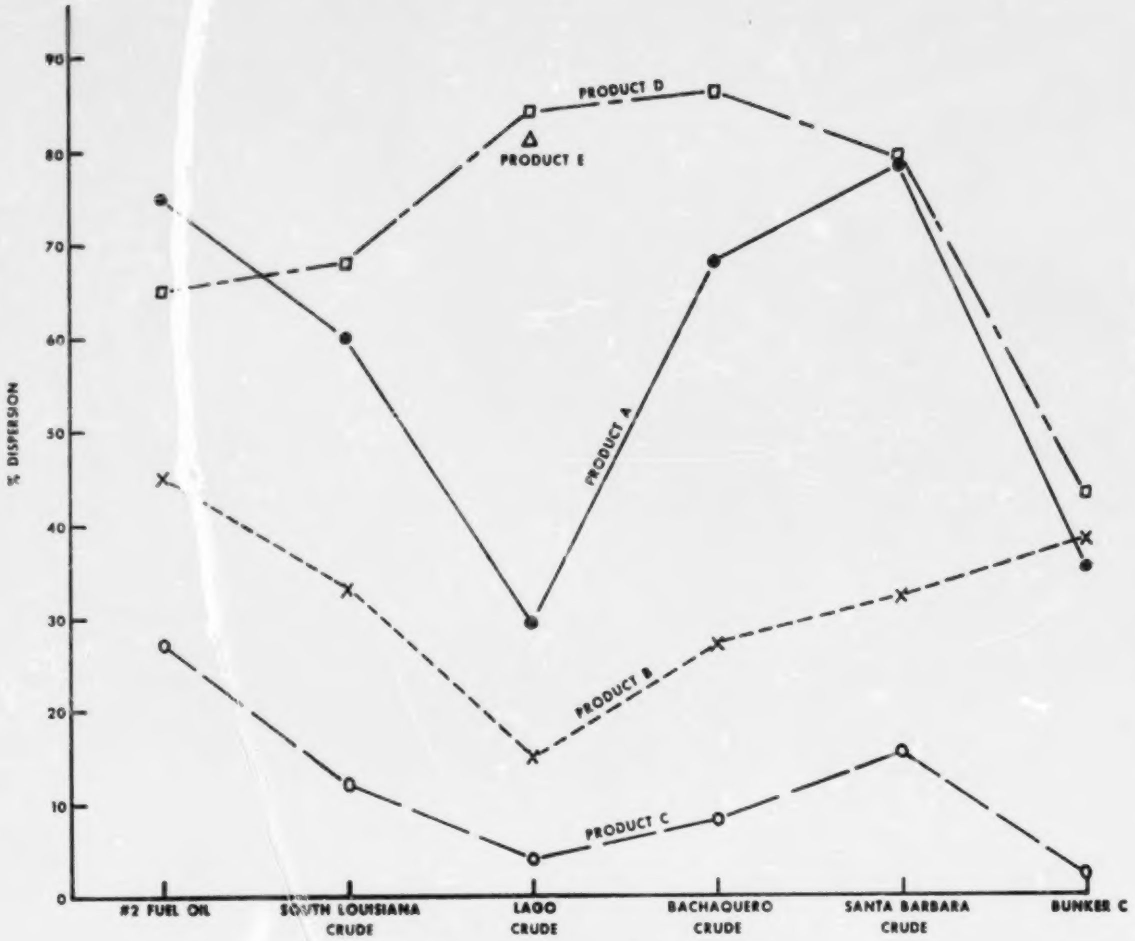
Obviously, we could not test all of the hundreds of products which have been marketed at one time or another as dispersants, but in an attempt to account for the properties of most of these products, we selected five dispersants which appeared to represent the types currently available (Table 2).[18] Product A is a typical solvent-emulsifier of the type used during the *Torrey Canyon*, with a typical non-ionic surface active agent and a petroleum solvent. Product E is similar, but with an anionic surface active component. Product B consists of a surface active agent similar to that found in Product A, but with a glycol based solvent. Product D is an alkanolamide. Product C contains a surface active agent which is an ester of fatty acids with polyhydric alcohols, in a solvent of water and short-chained alcohols.

These test oils and dispersants were used to examine the suitability of the tank test. The first observation concerned

TABLE 1. PROPERTIES OF TEST OILS

Oil Types	API°	Universal Viscosity 100°F	Pour Point°F	% Weight Sulfur	% Weight Asphaltenes	Neutralization Number	Volume % Distilled At		
							300°F	500°F	700°F
South Louisiana Crude	36.6	41	15	0.20	0.3	0.40	18	43	71
Lagunillas (Lago) Crude	17.7	1250	-5	1.92	8.5	2.2	5	15	34
Bachaquero Crude	17	1500	-5	2.2	7.0	2.7	6	17	35
Santa Barbara (Calif.) Crude	26	108	15	1.6	5.1	0.34	18	35	52
No. 2 Fuel Oil	32	35	-20	0.3		0.05	5	50	100
Bunker C	10	4500	60	2.5	10.0	2.5	0	5	20

Figure 2. Results of Navy tank test with different oils.



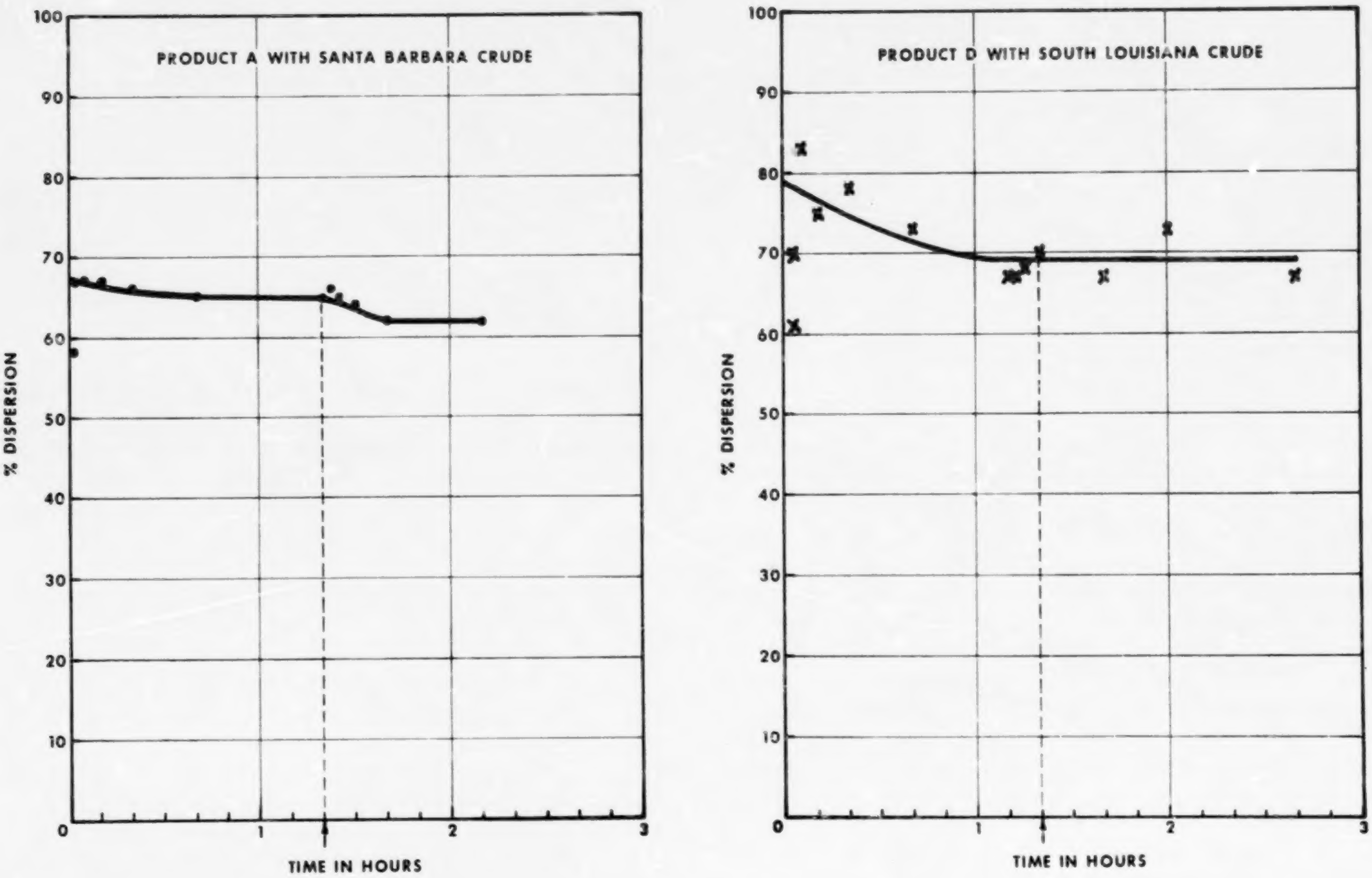


Figure 3. Dispersion stability in Navy tank test with no recirculation after 80 minutes (arrow at bottom of graph).

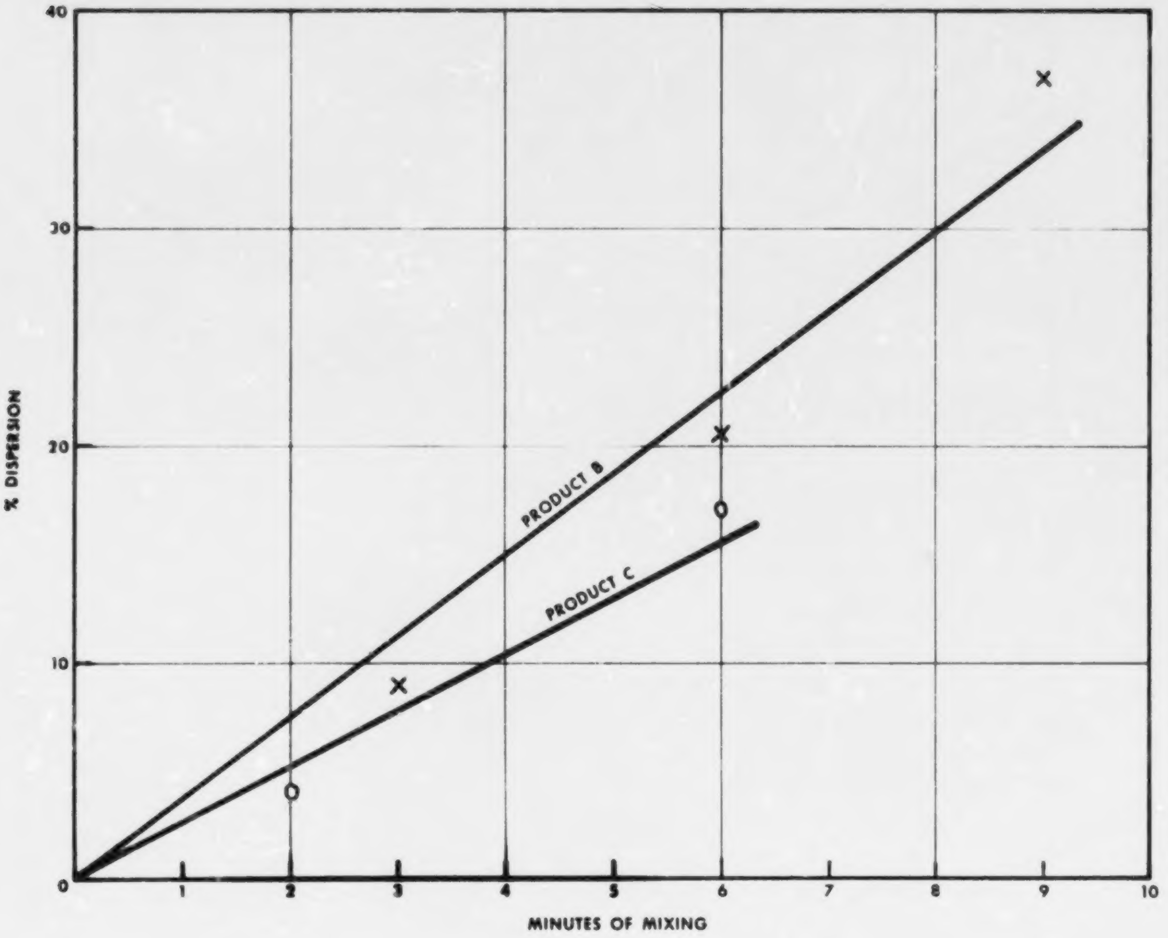


Figure 4.
Effects of mixing
Lago crude
when surface
was mixed with
eggbeater for one minute
contact time.

the effects of different oils, since the Navy procedure is limited to Navy Special Grade Fuel Oil. Figure 2 shows that results are significantly influenced by the type of oil used, which is to be expected. Dispersion obtained with this procedure was remarkably stable, as shown in Figure 3.

One factor which profoundly influenced dispersion efficiency was the nature of the contact between oil and chemical. Table 3 illustrates this. Increasing the time between the addition of chemical and the beginning of agitation from one minute to ten minutes increased the effectiveness of Product A three times, and decreased the effectiveness of Product B by one half. The performance of Product B was improved by confining the oil within a small ring within the main tank. This inner ring was designed to limit the oil to an area which it would normally cover under these conditions, thereby facilitating contact with the dispersant. Performance of Product B was further enhanced by adding it in a fine stream. All dispersants showed improved efficiency when mixed with the oil *prior* to placing on the water's surface. All of these results seemed to reflect the degree of mixing between oil and chemical before agitation.

In general, more agitation resulted in more dispersion (Figure 4) but slight variations in the time or conditions of hosing had negligible effects on the degree of dispersion.

Several chemical were tested by eduction into the hose stream. This involves aspiration of the dispersant into the stream of water in about a 6 per cent solution. The chemical is thus applied and agitated simultaneously. This failed to improve performance and, in fact, usually resulted in less dispersion than with the same amount of chemical applied in undiluted form and subsequently hosed.

Tests with different amounts of chemical indicated that dispersion was related to dosage in a roughly first-order, exponential manner (Figure 4). None of the chemicals tested reached optimum effectiveness at a ratio of chemical to oil of one to ten or less. Thus, 10 ml was selected as a standard quantity of dispersant for testing.

On the basis of these and other results the tank test was modified as follows:

1. Four test oils (Table 1) were used throughout.
2. A more complex salt solution was used for both tank contents and hosing. The Navy procedure used a solution of 3.5 per cent NaCl for the contents of the tank. Other ions, such as calcium and magnesium, which are found in sea water, were found to influence the performance of some dispersants. Thus, a synthetic sea water containing the major ions present in sea water, was formulated and shown to give results identical with natural sea water.

3. To facilitate contact between oil and chemical, a ring, 7.5 inches in diameter, was used to contain the oil, while chemical was added in a fine stream rather than being poured from a graduated cylinder. Also, the contact time between addition of chemical and agitation was lengthened from one to ten minutes.
4. Samples were withdrawn five minutes after the termination of hosing, which was found to be the shortest time required for the contents of the tank to stabilize.
5. 100 ml of test oil was used, but the amount of chemical was lowered to 10 ml to account for the increased effectiveness of dispersants now available.
6. A stability test was performed with the amount of chemical causing 50 per cent dispersion, thus making the stability determination independent of the degree of initial dispersion with 10 ml of chemical. This consisted merely of following the time course in the decay of initial dispersion (Figure 7).
7. A standard surface active agent was added to allow calibration tests from different laboratories.

With these modifications, the procedure provided the results shown in Figure 6. The modifications appeared to be sufficiently extensive to warrant a new name for the procedure–the Simulated Environmental Tank (SET) Test. Results were highly reproducible. Although this varied slightly with the chemical used, five replications with most chemicals yielded a mean value which had a 95 per cent probability of varying no more than 5 per cent.

TABLE 2.
APPARENT COMPOSITION OF TEST CHEMICALS

Product	Surfactant Ionic Nature[1]	Surfactant Basic Composition[2]	Solvent[3]
A	Nonionic	Ethylene oxide condensate of alkyphenol	Aromatic, aliphatic hydrocarbon, boiling point range similar to that of number 2 fuel oil
B	Nonionic	Ethylene oxide condensate of alkylphenol	Water, glycol
C	Nonionic	Polyhydric alcohol ester of fatty acid	Water, short-chained alcohol
D	Nonionic	Alkanolamide	Water
E	Anionic	Alkyl aryl sulfonate	Aromatic, aliphatic hydrocarbon, boiling point range similar to that of number 2 fuel oil

1. According to Weatherburn test.[19]
2. By infrared spectral analysis of dried (105°C) residue; test was not definitive, but results consistent with stated, presumed composition.
3. By distillation and infrared spectral analysis.

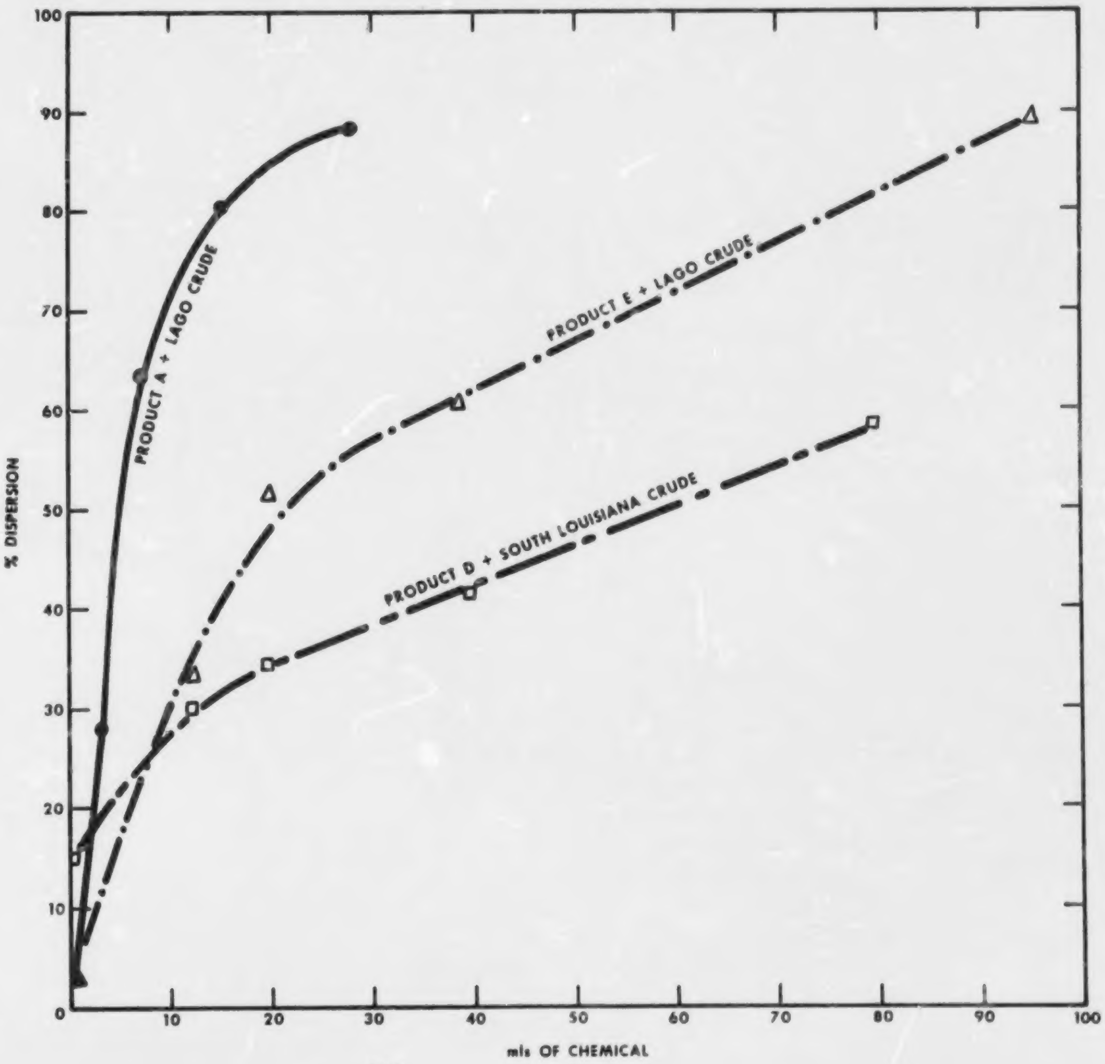


Figure 5. Dispersion with different amounts of chemical, according to SET Test procedure.

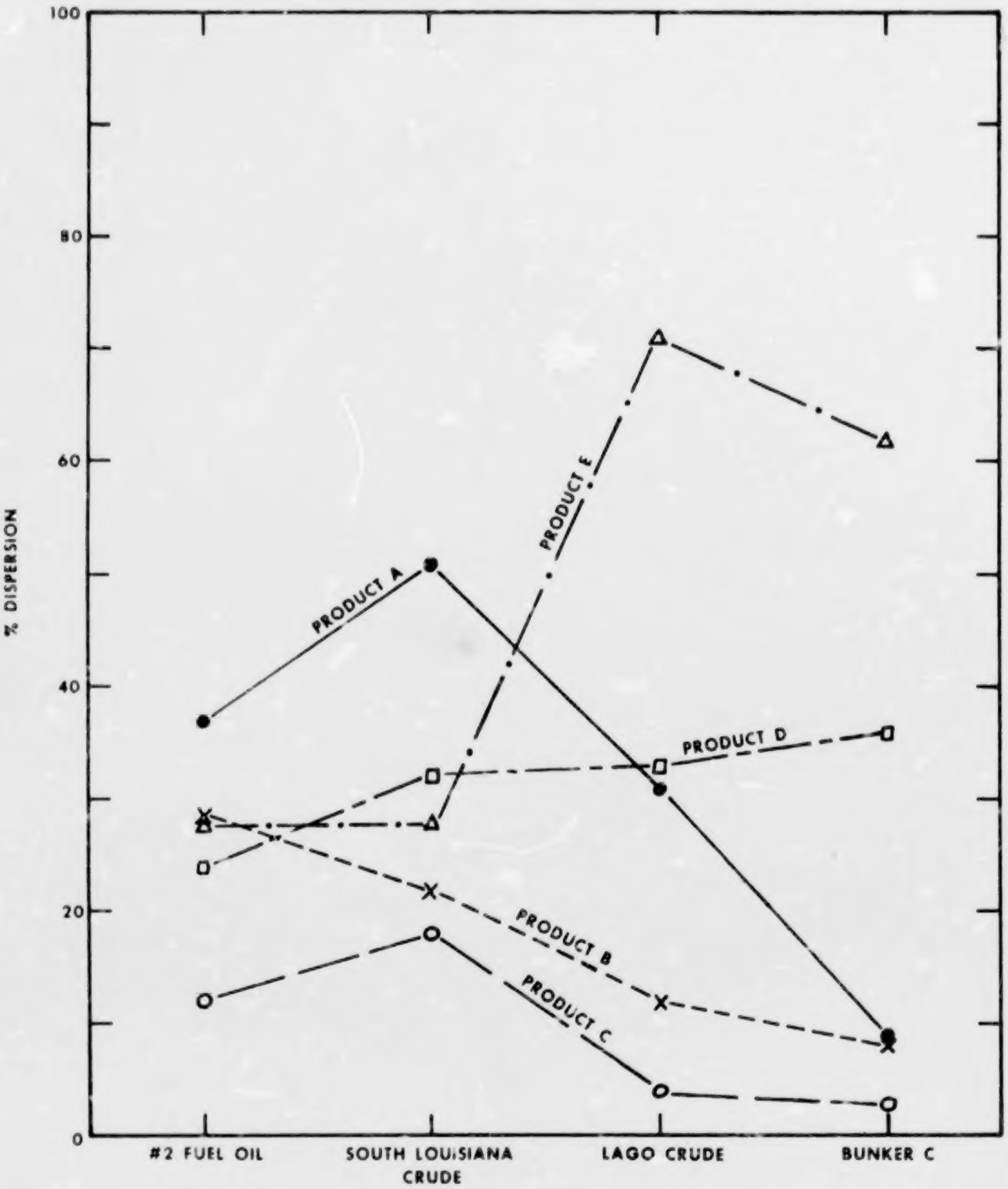


Figure 6.
Results of SET
Tests using
10 ml of chemical.

What, then, do these results shown in Figure 6 mean? We were confident we had selected test conditions reasonably representative of field conditions. But could we really say this test is any more meaningful than any of the others currently in use? The only way to find out was to move to the field, despite the many problems involved.

To do this we designed a simple field test. It began with a specially fabricated oil containment ring, eleven feet in diameter. Into this was poured the test oil, followed by dispersant in a fine stream from a pressurized fire extinguisher. After one minute, the mixture was agitated by the stream of a fire hose. During this, three observers, who were stationed on the deck of a vessel looking down on the test area, estimated the amount of oil on the water's surface after each step of the test. They were informed of the test only by code number and recorded their results independently. At the end of the test series, when results were compared, they showed a remarkable consistency among observers, and a good correlation with results of the SET test (Table 4). The difference in results with Products A and B between the field and SET tests can be explained by the longer contact time during the SET test, ten minutes as compared with one minute in the field, which increases the effectiveness of Product A and decreases the effectivness of Product B. The only remaining discrepancey between the field and SET test is the greater effectiveness in the field of Products C and D on No. 2 Fuel Oil and South Louisiana Crude, which could be related to the lesser visibility of these lighter oils.

During these tests we made a number of observations which relate to field use of dispersants. Condensed, they form a short list of recommendations:

1. Dispersants should be applied in undiluted form, in as fine a spray as the wind allows.
2. Eduction of dispersants into a hose stream is generally an ineffective method of application.
3. Time between addition of dispersant and agitation profoundly affects the resulting dispersion and should be adjusted to the properties of the chemical used.
4. The more violent agitation, the more dispersion.
5. Simple shake tube tests for visually demonstrating dispersant effectiveness are misleading. The color of the underlying water depends on the type of chemical used and comparison of the effectiveness of different chemicals by this means may not be valid.

Discussion

From these observations, and from what is already known, it is apparent that dispersion is a complex process which is influenced by a variety of factors. No single set of test conditions will produce results which account for the properties of all dispersants or which will apply to all field situations. A simple, quick laboratory test would be desirable, but for its design we would have to have answers to such questions as: "how stable an emulsion is required for effective dispersion?" or "how much mixing energy will produce an effective dispersion?" Until such questions can be answered, we must rely on empiricial tests such as the tank test described above. In the meantime this Simulated Environmental Tank Test, which provides results correlating well with field performance, at least to the extent field performance can be determined, and which simulates environmental factors, appears to offer a reasonable method for measuring dispersant effectiveness. The complete test procedure is described below.

Simulated Environmental Tank Test

1. Subject

This procedure applies to all materials which are to used for dispersing oils from the surface of water, primarily as a result of their action as surface active agents.

2. References

2.a. MIL-S-22864A (Ships), 24 February 1969, Solvent-Emulsifier, Oil Slick.

2.b. ASTM Specification D-396-67, Fuel Oils.

2.c. ASTM Specification D-93-66, Flash Point by Pensky-Martens Closed Tester.

2.d. ASTM Specification D-1298-67, Specific Gravity.

TABLE 3. EFFECT OF CONTACT TIME AND MODE OF ADDITION ON DISPERSOIN, LAGO CRUDE, NAVY TANK TEST

Test	A	B	C	D
1. 1 minute contact	29	23	4	84
2. 10 minute contact	90	13	2	82
3. 10 minute contact, ring	90	58	11	83
4. 10 minute contact, ring, fine stream	-	84	9	-
5. Premix	90	90	89	85

2.e. ASTM Specification D-445-65 Viscosity of Transparent and Opaque Liquids.

2.f. Cloud Point, *Standard Methods of Chemical Analysis, Vol. III-B*, Edited by F. J. Welcher, 6th Edition, 1966, D. Van Nostrand Co., Inc., Princeton, p. 1839.

2.g. Hardness by EDTA Titrimetric Method, p. 147, in *Standard Methods for the Examination of Water and Waste Water*, 12th Edition, American Public Health Association, Inc., N.Y.C., 1965.

3. Test

3.a. Apparatus: The apparatus to be used (see Figure 1) shall be that described in Paragraph 4.5.1.1. of Reference 2.a., except that the tank may be constructed from unpainted, stainless steel. In addition, use of a cylinder of stainless steel, 9" in length and 7.5" in diameter, which has been fitted with clamps so that it can be placed vertically in

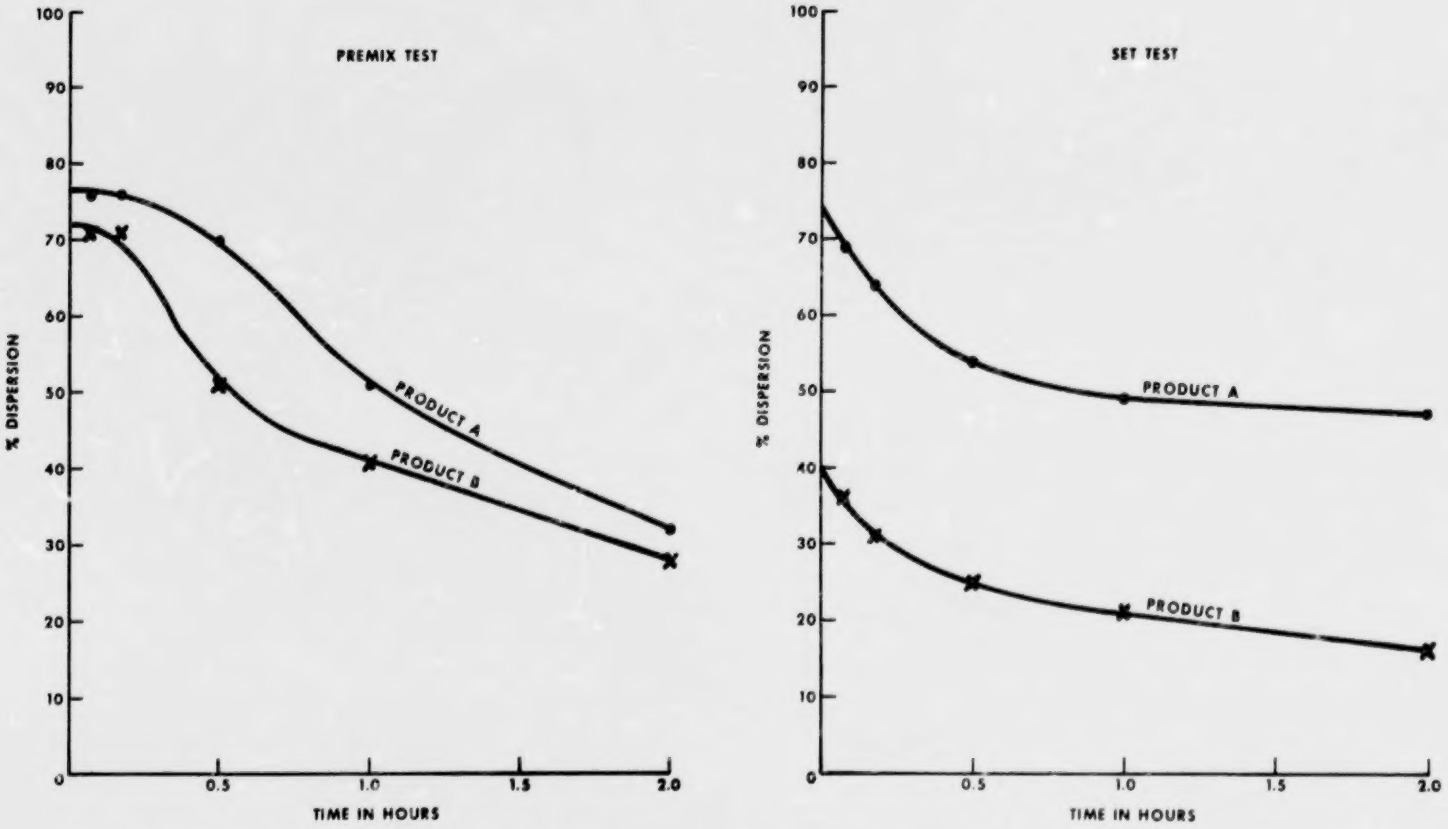


Figure 7. Dispersion stability in modified test tank for Lago crude. Chemical to oil ratio is 1/5 for product A and 1/4 for product B.

the center of the tank with its midpoint 16" above the base of the tank. Design the clamps to allow quick removal and replacement of the cylinder to and from the tank.

3.b. Oils: Test all chemical with 100 ml of each of the following oils:

3.b.1. No. 2 Fuel Oil, with characteristics defined in Reference 2.b.

3.b.2. No. 6 Fuel Oil, with characteristics defined in Reference 2.b.

3.b 3. Lagunillas Crude, with characteristics essentially as listed in Table 3.b.5.

3.b.4. South Louisiana Crude, with characteristics essentially as listed in Table 3.b.5.

3.b.5. Typical characteristics of Crude Oils:

	Lagunillas	South Louisiana
API°	17.7	36.6
Viscosity, Universal 100°F	1250	41
Pour Point, °F	-5	15
% Weight Sulfur	1.92	0.20
% Weight Asphaltenes	8.5	0.3
Neutralization Number	2.2	0.40
% Volume Distilled at:		
300°F	5	18
400°F	15	43
700°F	34	71

3.c. Standard Surface Active Agent: IGEPAL CO 630 (GAF Corporation, NYC) or equivalent as determined by formulation and cloud point (Reference 2.f.)

3.d. Salt Solution: Prepare with the following amounts of salts, and water of negligible hardness according to Reference 2.g. If necessary, adjust pH to 8.0 ± 0.1 with HCl or NaOH. The salinity should be 25 0/00. Use this salt solution for both hosing and for tank contents. This solution resembles the coastal sea water in composition of major ions.

Salt	g/l
NaCl	17.5
$MgCl_2$	3.6
Na_2SO_4	2.9
$CaCl_2$	0.82
$NaHCO_3$	0.15

3.e. Procedure: According to Reference 2.a., except with the following modifications:

3.e.1. Pour oil onto the surface of the water *within* the 7.5 inch diameter stainless steel cyliner; allow slick to stabilize.

3.e.2. Add chemical in a fine stream, through an aperture of 3 mm, contacting as much oil as possible; chemical must be applied during a time period of less than two minutes. (NOTE: A routinely available polyethylene laboratory spray bottle is suitable for this purpose. The fine tip may be cut off to expose a 3 mm opening. Exact amounts of chemical applied may be determined by weighing the bottle before and after application.

3.e.3. Wait ten minutes to allow the chemical to contact the oil.

TABLE 4. COMPARISON OF RESULTS FROM FIELD AND SET TESTS
Chemical to Oil Ratio is 1/2

Chemical	Oil	Set Test % dispersion	Field Test % dispersion
A	Lago Crude (Bachequero used in Field Test)	70	22
B		49	87
C		7	3
D		50	70
E		95	91
A	South Louisiana Crude	85	77
B		46	96
C		29	63
D		50	99
E		78	92
A	Number 2 Fuel Oil	62	88
B		80	91
C		22	80
D		47	95
E		78	90
A	Bunker C	31	17
B		26	65
C		6	2
D		60	65
E		95	90

3.e.4. Agitate the oil/chemical mixture with the salt solution according to Reference 2.a. Use a 1/2 inch inside diameter rubber hose with a 3/16 inch inside diameter outlet orifice, and water pressure of 50 pounds per square inch. Continue agitation until the water level reaches 18 inches.

3.e.5. At the termination of hosing, immediately start the recirculation pump; continue recirculation throughout the sampling period.

3.e.6. Sampling.

3.e.6.a. For determination of initial dispersion (3.e.11.a.) withdraw a sample five minutes after termination of hosing.

3.e.6.b. For determination of stability (see 3.e.11.b. for when to determine) withdraw a sample five minutes, fifteen minutes, thirty minutes, one hour, two hours, four hours, and six hours after termination of hosing.

3.e.6.c. Extract oil from samples according to Reference 2.a. and spectophotometrically determine oil concentrations at suitable wave lengths from standard curves of absorbance vs. oil concentration.

3.e.7. Blanks: Perform tests with chemical in the absence of oil. Measure samples at the same wave length as in the presence of oil. Subtract blank values so determined from all values obtained in the presence of oil.

3.e.8. Determine oil remaining in the graduated cylinder and on the walls of the stainless steel cylinder and thereby correct test results (this may be done by taking the oil up in solvent, diluting appropriately, and comparing absorbance with standard curves used in 3.e.6.c.).

3.e.9. Standard: Mix 2 ml of the standard surface active agent (3.c.) with 25 ml 2-methyl-2, 4 pentanediol (hexylene glycol) and add to 100 ml of test oil in a 250 ml separatory funnel. Shake this mixture vigorously for ten minutes, place on the surface of the water of the tank, without the stainless steel cylinder, and hose immediately. Sample as in 3.e.6. Initial dispersion should be as follows:

South Louisiana Crude,	55.3 ± 4.3%
Lagunillas Crude,	41.6 ± 3.2%

3.e.10. Maintain temperature at 23°C ± 2°C.

3.e.11. Chemical Dosage and Results:

3.e.11.a. Initial Dispersion: Determine the per cent dispersion of the total oil (100 ml less that adhering to the walls of the graduated cylinder and the 7.5 inch diameter stainless steel cylinder) caused by 10 ml of chemical. Report the mean of at least five replicate tests with this quantity of chemical.

3.e.11.b. Stability: Perform this test with the quantity of chemical (report this quantity) which produces 50% ± 5% dispersion. (If this quantity of chemical exceeds 100 ml, merely report this fact and do *not* perform the stability test). Sample according to 3.e.6.b. From a graph of per cent dispersion vs. time, using the curve of best fit, report the *time at which one-half of the amount of oil observed at five minutes remains.* If this value is not attained within six hours report the per cent dispersion at six hours.

4. Determine Flash Point of chemical alone according to Reference 2.c.

5. Determine Specific Gravity of chemical alone according to Reference 2.d.

6. Determine Viscosity of chemical alone according to Reference 2.c.

7. Additional information: Test *all* chemicals by the preceding procedures. *In addition* the results of any tests performed according to the preceding procedures, *except* with different contact time (3.e.3.) or method or amount of agitation (3.e.4.), which may be relevant to field use of the chemical tested, may be reported.

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Evaluation Of Dispersants

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Abstract

Chemical agents for treating oil pollution have been described variously as "detergents," "dispersants," "emulsifying agents," "solvent emulsifiers," and so on. In this paper, however, the word "dispersant" will be used to cover all such materials.

The basic way in which dispersants work is that they change the interfacial properties of oil and water, enabling an oil layer to be broken up by agitation into very small droplets which may be readily dispersed in the body of the sea. The ways in which dispersants are applied, and the available techniques for supplying agitation to the treated oil, differ greatly depending on whether or not the oil has come ashore. Very often, too, dispersants, which are effective in dealing with floating oil, are completely useless for cleaning beaches, although the reverse is seldom if ever true. There is a need, therefore, for separate methods of assessing the efficiencies of dispersants in combating oil at sea and on shore.

It is also necessary to know the effect of dispersant treatment on marine life, so that in alleviating the evil of oil pollution one does not cause unnecessary damage to marine flora and fauna. It is beyond the scope of this paper to discuss toxicity testing of dispersants. This subject has been covered by Dr. R. G. J. Shelton of the Shellfish Laboratory of the UK Ministry of Agriculture, Fisheries and Food. Rather, it is my purpose to describe what has been done by the Institute of Petroleum (IP) Working Party on "Detergents and their Application" to derive meaningful rules for determining which dispersants should be used for cleaning up oil pollution in various circumstances.

Laboratory Tests

The members of my IP Working Party are drawn not only from the oil and associated chemical industries but also from government departments. We started our tasks, therefore, fortunately but not fortuitously armed with the best available knowledge and practical experience in dispersant usage and testing. We knew so much, in fact, or at least thought that we did, that the specification of standard methods for assessing dispersant efficiency was expected to be little more than a formality. Three methods were already in widespread use:

1. A beach cleaning efficiency test, developed by the Ministry of Technology, Warren Spring Laboratory,
2. An emulsion forming efficiency test, devised at the Admiralty Oil Laboratory.
3. An emulsion stability test, based on one published in the Journal of the Institute of Petroleum (46, p 360, 1962) and modified by BP Refinery (Llandarcy) Limited.

We carried out a cooperative test program at six laboratories, using seven commercially available dispersants to check these methods for repeatability and reproducibility. When we got our test results, our confidence, although not broken, was severely bent. Different laboratories obtained widely different results from Tests 1 and 2 and, although Test 3 was more reproducible, it failed to distinguish adequately between products which were known to have different efficiencies in practice. Of course, in carrying out the test program, the participating laboratories suggest ways in which they might be improved. This knowledge was used to redraft all three methods, and the modified versions are given in Appendices 1, 2 and 3.

Appendix 1 describes the beach cleaning efficiency test in which a measured volume of fuel oil is spread on to a "beach" of glass balls, a dispersant is added, and the "beach" is washed with sea water. The efficiency of the dispersant is assessed by spectro-photometric determination of the percentage of oil removed from the "beach."

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TABLE 1. EMULSION CLEANING EFFICIENCY

DISPERSANT	LABORATORY	PER CENT FUEL OIL REMOVED FROM BEACH for dispersant : oil ratios of					
		$^1/_{10}$	$^2/_{10}$	$^3/_{10}$	$^4/_{10}$	$^5/_{10}$	$^6/_{10}$
A	a	15	23	48	57	35	37
	b	7	19	19	17	23	17
	c	16	21	38	40	68	36
	d	5	4	6	6	9	12
	e	3	6	6	8	10	11
	f	1	4	6	7	7	9
B	a	9	18	15	16	21	22
	b	9	33	31	30	45	39
	c	5	29	26	7	80	41
	d	3	4	5	5	7	7
	e	8	10	12	13	18	17
	f	5	11	11	11	13	15
C	a	3	4	6	8	8	9
	b	5	11	13	21	25	25
	c	5	14	17	33	65	55
	d	7	14	18	27	27	28
	e	3	3	5	10	10	11
	f	2	3	4	6	6	7
D	a	0	0	0	1	1	1
	b	2	1	1	1	1	1
	c	2	5	12	17	15	22
	d	0	0	1	1	1	1
	e	1	1	1	1	1	1
	f	1	2	2	1	1	1

Appendix 2 describes the emulsion-forming efficiency test in which crude oil is floated on sea water, dispersant is added, and the whole is gently swirled. The degrees of emulsification after certain time intervals are compared with a series of photographic standards to give a single rating number for efficiency.

Appendix 3 describes the emulsion stability test in which emulsions are produced by shaking mixtures of crude oil, sea water and dispersant, and the degree to which the emulsion has broken after standing for an hour is measured.

A further cooperative test program was carried out on these redrafted methods at the six laboratories, but this time limiting the number of dispersants tested to four. The results of these experiments are given in Tables 1, 2 and 3. They show that the hoped for improvements had not been achieved.

For example, in Table 1, where high values are indicative of good dispersant efficiency, there are many instances where the ratings given to a dispersant by separate laboratories differ by more than a factor of ten. Even for dispersant D, which is known by experience to be a very poor beach cleaner, one laboratory has rated it higher than several other laboratories rate the dispersants of proven efficiency.

Evidence that Test 2 is also unsatisfactory is given in Table 2. Here low values are indicative of good dispersant efficiency and even cursory examination of the data shows that opposite views of the effectiveness of the dispersants under test have been taken by different laboratories in many instances.

The results given in Table 3, although they suggest that the emulsion stability test is the most promising of the three under examination, also illustrate that the method is still unsatisfactory in its present form. Perhaps even more distressing than the lack of reproducibility of the methods is that the individual laboratories did not succeed in rating the dispersants in the same order of efficiency in the two series of cooperative tests.

The task of developing new laboratory methods for dispersant assessment is proceeding, making use of what experience and knowledge can be salvaged from the earlier work.

Field Tests

Even when repeatable and reproducible laboratory tests are available, it will be necessary to demonstrate that they can be related to practical pollution-clearance situations. Experience in the UK in dealing with the *Torrey Canyon* spill, in particular, but also with a large number of minor pollution instances, has given us considerable background knowledge of the relative efficiencies of various commercially-available dispersants.

Nevertheless, there is a need for field tests to confirm the laboratory findings for recently developed products. Two such tests are necessary to assess, once more, the efficiencies of dispersants in dealing with oil on shore and at sea. At the time of writing field trials have been planned and are imminent.

For the beach trial, a measured volume of oil is spread on to a shingle beach, dispersant is added, and the area is washed by the tide. The oil that is retained on the beach is assessed photometrically after extraction. The details of the test which was first developed by the Warren Spring Laboratory are given in Appendix 4. The sea trial is likely to prove far more difficult in practice and, although the procedure to be used has yet to be decided in detail, it is likely that the efficiency of oil dispersion will have to be assessed visually rather than by sampling and analysis.

Application of Test Results

No paper on dispersant evaluation would be complete without a short discussion on how the results of tests may best be used in practice. Even when one has, ideally, numerical ratings for the efficiencies of commercial products in dealing with floating and beached oil, the picture is not complete. Two other factors are of great importance—toxicity and cost effectiveness.

One should not accuse anyone of being mercinary merely because they want to consider closely the cost of a clean-up operation. Indeed, considerations of cost effectiveness could not only decide which dispersant should be used, but whether alternative clearance methods might be preferable. When one considers that there is frequently a factor of up to five or even ten, between the prices of commerical products, it can be seen that careful selection on a cost effectiveness basis is more than desirable.

Equally, one is not necessarily being callous or shortsighted if one says that the toxicity, or otherwise, of a product to marine life is not always the over-riding factor in choosing which dispersant to use in any particular instance. Choice is likely to vary depending on the location and circumstance of a pollution episode. In the open sea, the use of around 750,000 gallons of dispersant following the grounding of the *Torrey Canyon* was not noticeably injurious to marine life except in the extreme surface layers. Even on shore, where direct treatment with dispersant killed a large number of shore organisms of different kinds, the view was held that the preservation of coastal recreational amenities was of first priority.

So what should be advocated?

1. For the open sea, should one select a dispersant solely on considerations of cost effectiveness, ignoring toxicity?
2. Close to shore and in areas where there are, for example, important shellfish beds, should one choose a dispersant firstly for its lack of toxicity and only secondly on cost effectiveness?
3. On shore should one also make toxicity considerations of prime importance?

Perhaps, but no one would relish having to decide how much extra one is prepared to pay for pollution clearance in order to preserve a higher proportion of marine life. Until recently, even this unenviable choice was not often open, because non-toxic dispersants that were effective on shore were not available at any price.

New hope of carrying out pollution clearance using dispersants without damage to inter-tidal or sublitoral life has recently been raised by the announcement of a "non-toxic" product which is claimed to be efficient for use not only at sea but also on beached oil. Of equal import is the fact that this appears to have been achieved at a commercial price comparable to that of the most efficient toxic products. May it be the first of many such products which will make it practicable and economic to ban the use of toxic materials both on shore and at sea.

Having created a spirit of optimism, let us conclude on a cautionary note. In spite of all our expertise and experience we, in the United Kingdom, have yet to produce repeatable and reproducible laboratory tests for dispersant efficiency which can be related to practice. The development of such tests is getting nearer but let no one assume that they have been achieved until they have been proved to be meaningful in a statistically designed cooperative test program.

TABLE 2. EMULSION FORMING EFFICIENCY

DISPERSANT	LABORATORY	EMULSION RATING NUMBER for dispersant : oil ratios of								
		5/100	10/100	15/100	20/100	25/100	30/100	35/100	40/100	45/100
A	a	5	5	5	5	5	5	5	5	5
	b	10	9	9	7	5	5	4	3	5
	c	10	9	9	8	7	6	6	6	6
	d	7	7	7	5	1	1	0	0	0
	e	10	10	10	10	5	5	0	0	0
	f	7	5	3	3	3	3	2	2	2
B	a	7	6	5	5	3	5	5	6	6
	b	5	5	2	2	3	3	3	3	3
	c	4	4	2	0	2	2	2	2	2
	d	5	0	0	0	0	0	0	0	0
	e	5	5	2	0	0	4	5	5	5
	f	1	1	1	1	1	1	1	1	1
C	a	10	10	10	10	7	9	6	6	6
	b	7	7	6	5	5	6	6	5	5
	c	10	10	10	10	10	10	10	10	10
	d	5	5	0	0	0	0	0	0	0
	e	10	6	5	5	3	3	3	3	3
	f	7	6	1	1	1	1	0	0	0
D	a	10	9	7	6	6	6	6	4	4
	b	5	5	5	6	6	5	8	9	10
	c	2	2	5	5	5	5	5	5	5
	d	8	5	5	5	5	5	5	5	5
	e	10	10	10	10	10	10	10	10	10
	f	8	6	6	6	6	6	6	6	6

TABLE 3. EMULSION STABILITY

DISPERSANT	LABORATORY	PER CENT OIL IN AQUEOUS LAYER for dispersants : oil ratios of			
		1/8	1/4	1/2	1/1
A	a	52	66	74	64
	b	36	59	75	82
	c	56	62	39	51
	d	27	52	73	95
	e	52	63	66	64
	f	61	74	94	69
B	a	47	58	20	16
	b	62	63	40	64
	c	53	10	4	37
	d	28	33	63	87
	e	47	59	33	75
	f	41	62	31	53
C	a	56	80	92	66
	b	46	82	61	24
	c	57	71	14	33
	d	51	59	72	97
	e	36	66	58	36
	f	49	71	65	43
D	a	28	69	78	61
	b	68	68	60	50
	c	39	48	19	57
	d	45	55	52	57
	e	20	34	39	44
	f	36	17	33	69

APPENDIX 1

Test procedure 1

A Beach Cleaning Efficiency Test

A measured volume of oil is spread on to a "beach" of glass balls, dispersant is added, and the "beach" washed with sea water. Both the oil that is washed off the "beach" and that retained on it is collected and determined spectrophotometrically.

Apparatus required:

Glass funnels–parallel sided glass funnels 5 cm ID to contain beach material (Figure 1).
Stainless steel gauze–28 mesh B.S.S. in the form of close-fitting discs at base of funnels (Figure 1).
Syringe pipettes–two Jencon's Repettes, 2 ml capacity (Note 1).
Ballotini solid glass spheres–Jencon's No. 5, 16-25 mesch B.S.S.
Spectrophotometer–with 0.5 cm cells..
Separating funnel–1 litre.
Beakers–400-ml and 800 ml.
Measuring cylinder–100 ml.
Clock glass–4 cm diam with a 15 cm glass rod cemented to the concave surface.
Volumetric flasks–250 ml.
Hotplate.
Filter funnel–5 cm.
Filter papers–Whatman No. 1, 9 cm.

Reagents required:

Fuel oil–standard test fuel oil, viscosity of about 3000 seconds Redwood No. 1, stored at 25°C.
Chloroform.
Sea Water–synthetic sea water prepared from B.D.H. Sea Water Corrosion Test Tablets.
Chromic acid–a saturated solution of chromium trioxide in concentrated sulphuric acid.

Procedure:

Support the glass funnel in a clamp and insert the gauze disc. Measure out 100 ml of dry glass spheres in a dry measuring cylinder and pour into the funnel. Wash with 2 x 100 ml of sea water, allow to drain, and while the bed is still wet use the clock glass with the rod cemented to it, to press the bed down and to form a slightly concave surface.

Place a clean 800 ml beaker below the funnel. With the syringe pipette place 2.0 ml of fuel oil in the center of the bed, still wet with sea water. Allow the oil to soak into the bed for a period of one hour. At the end of this period add from another syringe pipette (Note 1) 0.2 ml (i.e., a ratio of 1:10) of the dispersant under test, distributing it dropwise and uniformly over the surface of the oil stain. Allow to stand for a further period of one hour.

Wash the bed with five consecutive 100 ml portions of sea water allowing the columns to drain after each washing. The final eluate should be quite clear (Note 2). Replace the 800 ml beaker with a clean 400 ml beaker and wash the bed with chloroform from a wash bottle until the eluate runs clear and the bed is visibly clean. At least 250 ml of chloroform should be used. It will be found advantageous to stir the bed occasionally during the chloroform extraction, to loosen any spots of oil that may remain in the bed.

Pour the contents of the 800 ml beaker into a 1 litre separating funnel and extract the oil with five successive 50 ml portions of chloroform, when all the oil should be extracted. Evaporate the chloroform extract on a hotplate to a volume of about 200 ml, cool, transfer to a 250 ml volumetric flask and dilute to the mark (Note 3). Filter the solution through a No. 1 filter paper into a 0.5 cm spectrophotometer cell and measure the absorbance at a wavelength of 580 nm.

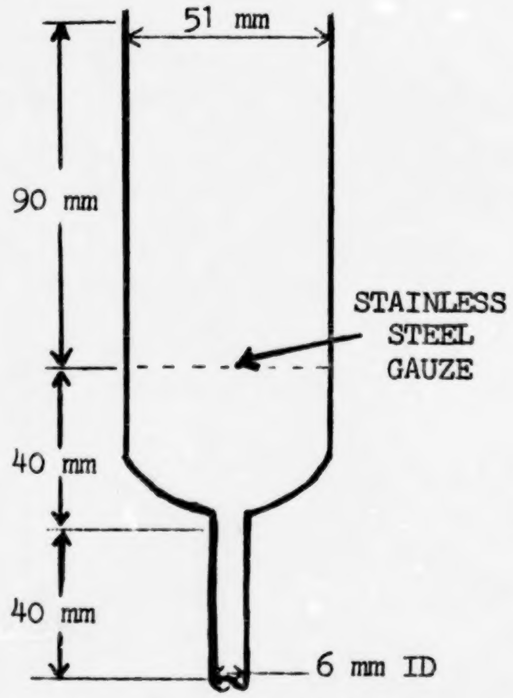


Figure 1. Beach cleaning efficiency test.

Pour the contents of the 400 ml beaker into a separating funnel and run off the chloroform layer. Extract the sea water left with two 50 ml portions of chloroform and add to the main chloroform solution. Evaporate this to a volume of about 200 ml, cool, transfer to a 250 ml volumetric flask and dilute to the mark (Note 3). Filter and measure the absorbance as above.

After each determination soak the glass spheres in chromic acid overnight, wash thoroughly with distilled water and dry before re-use.

Repeat the determination using 2:10, 3:10, 4:10, 5:10, and 6:10 ratios of dispersant to oil.

Calibration:

Using the syringe pipette measure three 2.0 ml volumes of oil into three separate beakers. Dissolve each portion of oil in chloroform, transfer to separate 250 ml volumetric flasks and dilute each to the mark. Measure the absorbance as before and calculate a factor for converting absorbance readings to volume of oil. Take an average of the three factors obtained.

Temperature:

Normal laboratory temperatures should be used (about 20°C). Keep away from direct sunlight.

Timing:

It is convenient to use a total of not less than six columns at one time. The total time taken for six concurrent tests is about four hours.

Results:

The results for each concentration of dispersant under test should be expressed as follows:

1. Volume of oil removed from the beach by washing with sea water: a ml.
2. Volume of oil remaining on beach after washing with sea water and recovered by washing with chloroform: b ml.
3. Total volume of oil recovered: a + b ml.
4. Percentage of oil removed from beach $\frac{a}{a+b} \times 100\%$.
5. Ambient temperature at which the test has been made: °C.

Notes:

1. The syringe pipette for oil, is used without a needle. That for solvent emulsifier is filled without a needle, but a short needle of suitable bore (usually a No. 16 needle) is fitted before the delivery of the required quantity of dispersant. With viscous materials, a larger bore needle will be required.
2. If the eluate is not clear, wash with a further two 50 ml portions of sea water and combine the eluates.
3. The chloroform solution should be perfectly clear after the evaporation, and should remain clear on dilution. If clouding occurs, boil gently for a few minutes, again allow to cool and dilute to volume.

APPENDIX 2

Test procedure 2

An Emulsion Forming Efficiency Test

In this test, crude oil is floated on the surface of salt water in a small beaker and a measured amount of dispersant added. The beaker and contents are gently swirled and observations of the state of the contents, taken every hour, are compared with the state of the contents of a series of standards as shown in a series of photographs. These observations taken over a period of five hours are used to give a single rating number. A series of nine beakers is used, and the dispersant to oil ratio is varied from 5:100 to 45:100.

Apparatus required:

Beakers, pyrex, squat form, 100 ml capacity.
Measuring cylinder, 50 ml.
Syringe pipettes, two Jencon's Repette, 2 ml, (Test Procedure 1, Note No. 1).
Rotating table, rototest table (Luckham & Co. Ltd) modified to hold 18 beakers securely, (Figure 2). The deck of this table rotates with a fixed amplitude of 4 cm., and should be set to give 120 rpm when fully loaded.

Reagents required:

Sea water, synthetic sea water prepared from B.D.H. Sea Water Corrosion Test Tablets, used at 20°C.
Crude oil, Kuwait crude oil, a selected material, set aside for this purpose.
Chromic acid, a saturated solution of chromium trioxide in concentrated sulphuric acid.

Procedure:

Soak the beakers overnight in chromic acid, wash in tap water, then in distilled water and dry in an oven. Measure 50 ml of sea water into each of 9 beakers and pipette 2 ml of crude oil on to the surface of each.

Pipette 0.1 of the material under test on to the surface of the oil in the first beaker (i.e., 5:100 dispersant to oil ratio), 0.2 ml into the second beaker and so on up to 0.9 ml (i.e., 45:100 dispersant to oil ratio) in the ninth beaker.

Set the deck of the Rototest table in motion for 30 minutes before it is required for the test, to enable the deck to reach constant speed, and set this to 120 rpm.

Insert the beakers into the holes in the deck of the table and swirl at 120 rpm for a period of one hour. Stop the table momentarily, quickly remove one of the beakers from the deck for examination and set the table in motion again immediately. Examine the contents of the beaker, by comparing it with the standard photographs. This *must* be

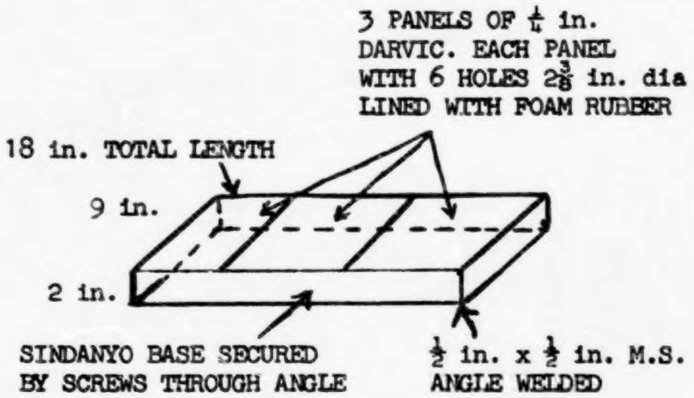

3 PANELS OF ¼ in. DARVIC. EACH PANEL WITH 6 HOLES 2⅜ in. dia LINED WITH FOAM RUBBER
18 in. TOTAL LENGTH
9 in.
2 in.
SINDANYO BASE SECURED BY SCREWS THROUGH ANGLE
½ in. x ½ in. M.S. ANGLE WELDED

Figure 2. Modified top for rototest apparatus.

carried out rapidly, as some separation may take place, particularly at the lower dispersant concentrations. The contents of the beaker should be rated according to the following classification (Figure 4):

Rating 1. Complete emulsification with negligible oil floating on the surface.
Rating 2. Some emulsification but with oil still floating on the surface.
Rating 3. Negligible emulsion formation–sea water clear.

Return the beaker to the swirling table and assess the rating of each remaining beaker in turn. Repeat the swirling for a further four hours making observations at the end of each hour. For each beaker, record all the ratings observed and report the sum of these ratings minus five, this figure being called *the Rating Number*.

Temperature:
The test should be made at normal room temperature (about 20°C), and out of direct sunlight.

Timing:
Using the modified deck to the Rototest table, two samples of dispersant can each be tested at the nine different concentrations in a period of about six hours.

Results:
The results should be reported as follows:

1. The Rating Number for each concentration of dispersant as shown in Figure 3 below.
2. The ambient temperature at which the test has been conducted: °C.

APPENDIX 3

Test procedure 3

An Emulsion Stability Test

This test is designed to measure the stability of the oil-sea water emulsion produced with oil and dispersants. This is carried out by measuring the extent to which the emulsion has broken after standing for a period of one hour.

Apparatus required:
Separating funnels–2 litre, spherical.
Conical flasks–50 ml and 250 ml, glass-stoppered.
Syringe pipettes–two, Jencon's Repette, 10 ml, (Test Procedure 1, Note 1).
Measuring cylinders–100 ml and 1 litre.
Volumetric flasks–250 ml.
Beakers–250 ml and 600 ml.
Mechanical shaker–this could have a vibrating mode of action (Note 1): (a BTL model No. 330/0012 is suitable).
Spectrophotometer–with 0.5 cm cells.
Hotplate.
Filter funnel–5 cm.
Filter papers–Whatman No. 1, 9 cm.

Reagents required:
Standard oil, standard fuel oil, viscosity about 3000 seconds Redwood No. 1. Stored at 25°C.
Sea water, synthetic sea water prepared from B.D.H. Sea Water Corrosion Test Tablets, used at 20°C.
Chloroform.

Procedure:
Using the syringe pipette transfer 4 ml of oil to a 50 ml conical flask. Similarly add 2 ml of the dispersant under test, stopper the flask and mix thoroughly using the mechanical shaker (Note 1). Pipette 2 ml of this mixture into a 250 ml conical flask already containing 50 ml of sea water, stopper and shake vigorously by hand for 30 seconds. Pour contents of the flask into the 2 litre separating funnel containing 1 litre of sea water. Add a further 50 ml of sea water to the 250 ml conical flask stopper, shake and pour the contents into the 2 litre separating funnel. Stopper the funnel and shake vigorously by hand for 30 seconds. Set the funnel aside for one hour.

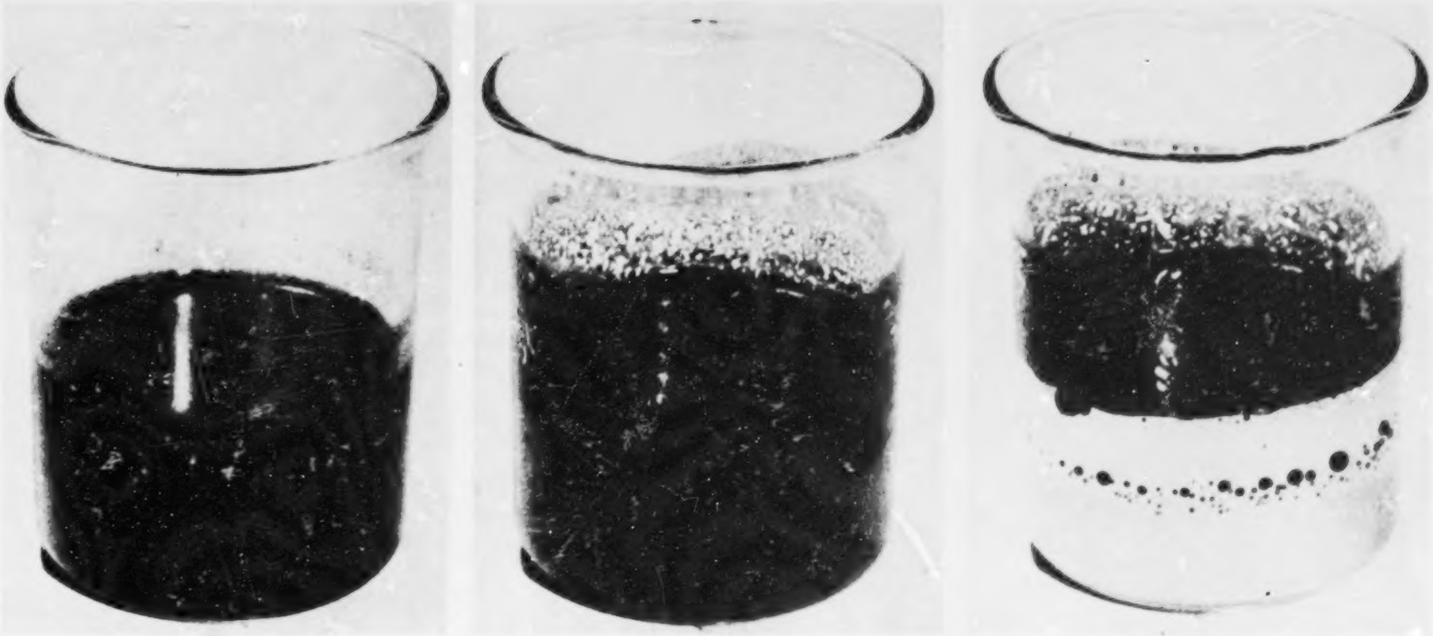
At the end of the hour, run off the lower aqueous layer containing emulsified oil into a second separating funnel, leaving the oil layer behind. Extract each layer with five 50 ml aliquots of chloroform when all the oil will have been removed and colourless extracts obtained. Collect the extracts from each layer in two separate 600 ml beakers. Evaporate each chloroform solution on the hot plate until the volumes are below 200 ml, cool and transfer to separate 250 ml volumetric flasks. Dilute each to the mark with chloroform, filter into a 0.5 cm cell through a dry No. 1 filter paper and measure the absorbance of each solution at a wavelength of 580 nm (Note 2).

Repeat the test with 1:8, 1:4 and 1:1 ratios of dispersant to oil using additions of 0.5, 1 and 4 ml respectively of dispersant to 4 ml of standard oil in a 50 ml conical flask.

Calibration:
Using the syringe pipette transfer 2.0 ml of oil into each of three 250 ml beakers. Dissolve each portion of oil in about 100 ml of chloroform, transfer to separate 250 ml volumetric flasks and dilute each to the mark. Measure the absorbance of each against a chloroform blank at 580 nm in 0.5 cm cells. Calculate a factor for converting absorbance readings to volume of oil, and take an average of the three factors obtained.

Ratio of dispersant to oil:	5:100	10:100	15:100	20:100	25:100	30:100	35:100	40:100	45:100
Rating Number:									

Figure 3. Method of recording rating number for each concentration of dispersants.



Rating Number 1

Rating Number 2

Rating Number 3

Figure 4. Rating No. 1 shows a complete emulsification with negligible oil floating on the surface. Rating No. 2 shows some emulsification but with oil still floating on the surface. Rating No. 3 shows negligible emulsion formation with sea water clear.

Temperature:

Normal laboratory temperature should be used (about 20°C). Keep away from direct sunlight.

Timing:

Using five separating funnels and staggering the tests by 30 minutes, four tests on one sample can be made per day.

Results:

The results should be expressed as follows:

1. Volume of oil recovered from the aqueous layer: c ml.
2. Volume of oil recovered from the oil layer: d ml.
3. Total volume of oil recovered: c + d ml.
4. Percentage oil recovery in the aqueous layer: $\frac{c}{c+d} \times 100\%$
5. Quote the ambient temperature at which this test has been conducted: °C.

Notes:

1. In an earlier series of tests, difficulties were experienced in some laboratories in obtaining complete mixing when shaking by hand, particularly with aqueous-based materials. For this reason, the use of a mechanical shaker is suggested. Adequate results may be obtained by pipetting into a small beaker and stirring vigorously with a short, stout glass rod.
2. The chloroform layer should be perfectly clear. If clouding occurs, boil gently for a few minutes, again allow to cool and dilute to volume.

APPENDIX 4

Procedures For A Field Beach Cleaning Efficiency Test

A series of 4 ft. 3 in.-sided squares is marked out along the length of a shingle beach, parallel to the tide front, with a three-yard spacing between the sides of adjacent squares.

A hole is dug in the center of each square and a wire mesh basket, 1 ft. x 1 ft. square x 9 in. deep (about ¼ mesh) is sunk into the hole. The shingle is replaced in and around the basket so that the top of the basket is flush with the general level of the beach.

The marked areas are carefully wetted by pouring on sea water from a bucket.

125 ml of fuel oil, viscosity ~ 3000 Redwood seconds at 100°F, is poured as evenly as possible onto the shingle within the square foot of basket area. One-half gallon, less 125 ml, of the same oil is poured as evenly as possible over the remainder of the test area and mixed with the surface shingle by hand. The above application rate produces an oil layer equivalent to an even distribution thickness of about 0.136 cm.

Each test area is then carefully and evenly sprayed with one pint of the dispersants under test, using standard equipment.

The tide is then allowed to wash over the test strip and recede. Visual examination and record is made of the appearance of each area and the baskets and their contents removed and placed in plastic bags for subsequent laboratory examination. This involves extraction of the oil from the shingle with chloroform and measurement of the oil retained by a suitable procedure, e.g., spectrophotometrically.

The test is normally carried out using two plots per dispersant and including two blanks, with a randomised distribution.

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Chemical Treatment Of Oil Spills

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Abstract

Chemical treatment methods have been used at all recent major oil spills with varying degrees of success. It is the intention of this paper to bring to light the latest technical information on the applicability and effectiveness of the various chemicals and materials presently available for preventing and or controlling oil spills. Special emphasis is given to techniques designed to absorb and gel oils floating on the water surface, to sink oils, and to permit burning of the oil mass upon open waters and affected shorelines.

The impact, consequences and damages of small and large oil spills are covered by other prominent speakers at this Conference, and therefore, will be only briefly mentioned as necessary.

Absorbent, adsorbent, "sorbent" materials–these products are defined in rather loose terms partly because of the wide variety of compounds available, and the many interactions possible with oil spills. The word "sorbent" may apply to any material which entrains or entraps oil, or a substance onto which oil adheres to the surface. The terminology may also refer to the process of agglomerating or gelling oils, or to the act of combining oil with an oil sinking agent prior to the oily mass dropping below the water surface. Regardless of what definition is used, all good sorbent materials are considered to be both oleophilic-oil attracting–and hydrophobic-water repelling.

Oil sorbents may be divided into three general classes by origin:

1. Naturally-occurring products
2. Modified or chemically-treated natural products
3. Synthetic or man-made

The natural products may be further subdivided into materials of vegetable, mineral and animal origin. Sorbents may also be classified in other ways based upon their composition or physical form, such as:

1. Powdery products
2. Granular materials
3. Fibrous materials
4. Pre-formed plastic-type slabs or sheets
5. Synthetic foams generated at the time and place of use.

Types of floating sorbent materials presently available are:

1. *Natural Origin.* Types derived from vegetative sources comprise straw, hay, seaweed, kelp, ground corn cobs, natural grasses, wood bark, ground bark, sawdust, reclaimed fibers from paper processing, and peat moss. Types derived from mineral sources may include the various clays, including montmorillinite, kaolin, fuller's earth, diatamaceous earth, etc.; vermiculite and the other micas; many forms of silicates; perlite; pumice; and asbestos. Sorbents of animal origin include chrome shavings from leather processing, wool wastes, feathers, and textile wastes.
2. *Modified Natural Products.* These materials comprise most of the sorbent types mentioned above but are chemically-treated to produce a more desirable result. Some of the modified types are expanded perlite, charcoal, stearate-coated talc, asbestos treated with surfactant, and sawdust and vermiculite coated with silicones.
3. *Synthetic Products.* These sorbents include a vast array broadly categorized as plastics and rubber, but more specifically as the polyurethanes, polypropylenes, ethylenes, styrenes, resins, polymers, and co-polymers.

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Sorbents are deployed for the purpose of attracting and agglomerating an oil slick with the intent of limiting the movement of oil and facilitating cleanup. Up to the present time, straw, particularly that from wheat stalks, has been the main sorbent used in oil spills because of its availability, relatively low cost, non-toxic nature, and accepted effectiveness. The group of sorbent products derived from the synthetics or plastics manufacturing area holds considerable promise because of the high oil pick up ratios. However, because of their high costs and the many operational-use problems to be solved, their application has been limited.

An important point to be made concerning sorbents is that many of the natural and modified materials which are reported as floating agents, will in fact, create a gelatinous mass with an inherent tendency to sink to the bottom of the water body. In many cases these floating sorbents will start to sink after entraining only minimum amounts of oil. If surface harvesting of the sorbent-oil mass is anticipated, and instead the oil sinks, the end result may not only be unwanted, but may cause severe ecological damage. During recent oil spills, both talc and small quantities of straw have been observed to sink when bound with heavy oil.[1]

There is a dearth of comparative data on performance and oil pick-up by floating sorbents, particularly under actual oil spill conditions. Data presented in Table 1, which shows the cost-effectiveness of various sorbents, have been obtained primarily from the literature, manufacturers, and from inhouse research efforts at the Edison Water Quality Laboratory. These figures are based upon approximations of oil absorbance ratios and unit costs of materials secured at the point of supply. There is great need to develop, under actual field conditions, more precise information on the comparative effectiveness and efficiency of sorbents. In this regard, FWPCA's Edison Water Quality Laboratory is presently attempting to develop standard test procedures by which sorbent materials can be rated by interested agencies.

The first group of sorbents in Table 1, which are primarily derived from forestry products, are relatively low in purchase costs. However, because of lesser efficiency in oil pickup, it is implied that greater amounts of these sorbents will be necessary, together with higher transportation and handling costs in a typical cleanup operation. The plastics or synthetics demonstrate good pickup efficiencies but unit purchase costs are quite high, thus making those responsible for cleanup shy-away from these materials. Large volume production and greater attention by the chemical manufacturers to the many possible uses of synthetics in the water pollution control field could significantly reduce the unit costs and increase their use during oil cleanup.

It must be noted that costs in Table I are given for *sorbent materials only*, and as such, represent a small portion of the total costs incurred in actual cleanup. Other important costs must cover transporting the raw materials to the site; the various equipment, manpower and auxiliary appurtenances necessary at the site; associated amortization, operation and maintenance, overhead, fringe benefits, etc.; lease or purchase of surface craft; and providing for other elements of the cleanup operations such as physical booms, mechanical pickup and the safe disposal of recovered oily masses.

A report recently compiled by the Battelle Northwest Research Institute for the U.S. Navy on methods for removing oil from harbor waters, gives cost analysis and effectiveness studies for total systems cleanup.[2] Two of the systems are described as: 1) use of sorbents plus manual retrieval and containment, and 2) sorbents plus portable suction devices and containment. Cleanup costs, and we stress once again *total costs*, for cleaning up recurring oil spills in harbors were calculated as being $1.60–$2.65 per gallon of oil removed by the first systems approach, and $1.35–$3.00 per gallon of oil removed by the second approach. These two systems compared favorably to others considered.

Sorbents, whether employed in a simplified operation or as part of a large operation, continue to have high expectations in oil spill control and cleanup. However, as for other approaches, many questions and problems still remain. Sorbents must be visualized integral with the total systems approach. In other words, what is the nature and disposition of various sorbents through each step of the operation? What are the practical and economic limitations and constraints? Will the absorbents work properly or will they serve to create even more difficulties and additional costs? Dumping large quantities of sorbents in the proximity of an oil slick may do little to assist oil cleanup. Proper techniques and equipment are lacking for evenly distributing large quantities of sorbents over wide expanses of open water; for properly agitating and mixing the sorbent with the oil mass; and for harvesting the oily agglomerate from many acres or square miles of water surface. Even assuming prompt and feasible recovery, which we know does not exist with today's technology, we face the problem of having shoreside facilities and adequate land areas for convenient and safe disposal (or re-use) of many hundreds of tons of oily masses. In landfill disposal, strict provisions must ensure that groundwater contamination does not occur and stormwater runoff and drainage does not contaminate adjoining land areas. Open burning as a possible disposal alternative seems very objectionable.

It is known that environmental conditions and the nature, viscosity, age and degree of weathering of the spilled oils will greatly determine sorption efficiency. Difficulties have been found with various sorbents for attracting heavy and weathered oils. Most sorbents will require significant agitation with the floating oils and many are time-dependent at least over the first 15 minutes. The total cleanup system involving sorbents becomes increasingly complex with the larger oil spills. Toxicity associated with sorbents would seem minimal compared with chemical emulsifiers, if the material is judiciously selected for retaining its integrity in water. The largest problem with the sorbent system is the recovery of the oily masses. Although past experiences with straw may be termed successful, this process is slow, tedious, dirty, and relatively expensive since a large manpower force is required for harvesting. On a West Coast spill early this year, it was reported that no truly satisfactory at-sea method was found to recover the agglomerated oil-straw mixture from the water surface. It seems highly probable, however, that in the near future, harvesting equipment, including automated mechanical

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[1] Superior numbers refer to literature references at conclusion of text.

TABLE 1. FLOATING SORBENT MATERIALS — COSTS IN CLEANUP OF 1000 GALLON OIL SPILL[A]

Type Material	Pick Up Ratio Weight Oil Pick Up Weight Absorbent	Unit Cost Absorbent $ (Ton Absorbent)	$ Cost of Absorbent for Cleanup of 1,000 Gals. Oil Spill[B]
Ground pine bark, undried	0.9	6	27
Ground pine bark, dried	1.3	15	47
Ground pine bark	3	–	–
Sawdust, dried	1.2[C]	15	50
Industrial sawdust	–	56	–
Reclaimed paper fibers, dried, surface treated	1.7	30	75
Fibrous, sawdust and other	3	–	–
Porous peat moss	1.0	–	–
Ground corn cobs	5	30	21
Straw	3–5[D]	30	27
Chrome leather shavings	10	Indicated comparable to straw in cost.	
Asbestos, treated	4	500	440
Fibrous, perlite, and other	5	416	290
Perlite, treated	2.5	230	320
Talcs, treated	2	70 – 120	120 – 210
Vermiculite, dried	2	–	–
Fuller's earth	–	25	–
Polyester plastic shavings	3.5 – 5.5	100	80
Nylon-polypropylene rayon	6 – 15	–	–
Resin type	12	3,100	900
Polyurethane foam (Ref. 1)	70	20,000	1,000
Polyurethane foam (Ref. 2)	15	4,500	1,050
Polyurethane foam (Ref. 3)	70	–	–
Polyurethane foam (Ref. 4)	40	2,260	195
Polyurethane foam (Ref. 5)	80	1,200	55

[A] Bibliography (1, 2, 3, 4, 5, 6, 7, 8, 13, 14)
[B] Does not include delivery, application and labor costs
[C] Another reference gives a ratio of 20
[D] Other reports have indicated ratios of 20 and above

equipment for collecting and removing the sorbent-oil agglomerates,[1, 2] can be adapted to oil spills.

Oil Sinking Agents. These are oil-attracting and water-repelling sorbent materials designed to sink oil slicks out of sight rather than agglomerating oil on the water surface. It was previously described that certain sorbents have the tendency to float and sink simultaneously which is considered detrimental in oil spill cleanup. The use of oil sinkants would seem advantageous in deeper waters outside heavy fishing zones, such as off the continental shelf and where adverse effects upon biological bottom life may be held at a minimum.[8]

Oily discharges into inland rivers and coastal waters do not remain floating forever since much of the oil will be naturally absorbed onto clay, silt and other particulate matter normally suspended in the water, thus causing eventual sinking of the oil. Sinking by natural means, for example, is believed to be one of the primary causes for the disappearance of oil slicks in the New York Harbor complex.

Various types of natural materials and commercial products are presently available which are claimed to be effective in sinking oil slicks. Typical agents include sand, brick dust, fly ash, china clay, volcanic ash, coal dust, cement, stucco, slaked lime, spent tannery lime, carbonized-siliconized-waxed sands, crushed stone, vermiculite, kaolin, fuller's earth, and calcium carbonate, including the "Oyma" type chalk used during the *Torrey Canyon*.

Sinking agents are believed most efficiently employed on thick, heavy and weathered oil slicks in contrast to relatively light and fresh oils. These agents are granular or fine particulate solids with a specific gravity generally between 2.4 and 3.0. These agents must be evenly distributed over the surface of a slick and supplied with proper mixing, agitation and time interaction. The particle-coated and agglomerated mass eventually becomes heavier than water and sinks to the bottom.

The major problem in sinking oils is that the bonding of the agent with the oil must be nearly permanent. Experiments in both the laboratory and field show that many agents will release entrapped and sunken oils back to the water environment. Increasing the application rate two or three times over prescribed amounts has served to minimize this release.

Studies conducted by various investigators[4, 9, 10, 12] has indicated that:

1. Sulfurized oils may show greater sinking abilities than desulfurized oils because of higher potentials for hydrogen bonding.
2. When sands are used for sinking it may be expected that the oily mass will be stable under water when the sands are closely packed and the interstices are filled with oil giving an oil content around 40 percent and a bulk density about 1.7. However, when the sands are loosely packed, the mass will become internally mobile so that oil drops will

TABLE 2. OIL SINKING AGENTS, APPLICATION RATES AND OTHER OPERATIONAL DATA[A]

Type Material	Application Ratios (Weight Sinking Agent: Weight Oil Treated)	Comments
Silica, untreated	----------	Released oil easily after sinking
Carbonized sand	1:1 to 3:1	Higher proportion of sinking agent considered most appropriate; $27/ton carbonized sand (1948); specific gravity particles = 2.7
Sands, amine-coated	3:2 to 2:1	Large-scale application costs estimated $5 – $10 per ton of oil treated
Sands, 0.5% silicone coated	----------	More effective on heavier oils
Fly ash, untreated	----------	Released oil easily after sinking
Fly ash, 0.5% silicone coated	2:1 ratio or higher	Permanent oil sinking reported; more effective on lighter oils.
Spent tannery lime	----------	Good oil retention properties after sinking
Kaolin clay	----------	Released oil easily after sinking
Bentonite, montmorillinite clay, treated and untreated	----------	----------
Calcium carbonate	----------	Released oil easily after sinking
Fuller's earth	1:1 to 9:1	1:1 to 3:1 for sulfurized oil; 3:1 to 9:1 for desulfurized oil.
Calcium carbonate – Champagne chalk treated with 1% sodium stearate	Approx. 1:1	Used off the coast of France during the Torrey Canyon; $60 – $80/ton sinking agent. Specific gravity particles – 2.7.
Synthetic silicate	----------	High efficiency in absorbing fuel and crude oils; some difficulty in sinking the mass.
Synthetic plus filler material	4:3 or higher	Estimated $120/ton sinking agent.

[A] Bibliography (2, 3, 4, 9, 10, 12, 13, 14)

separate and escape to the water until equilibrium is re-established.

3. With carbonized sand, it was indicated that up to three pounds of sand would be required to sink one pound of oil. Large-scale applications of amine-coated sands envision spraying the sand in a slurry form from a large vessel or hopper dredge.

In ports and harbors it has been mentioned that turbulence or agitation of the water body caused by storms or passing vessels may tend to release oily masses previously sunk. For siliconized sand, it has also been suggested that one-per cent bone flour or an inexpensive fertilizer may be added to promote bacterial growths and accelerated decomposition of the sunken mass.[2, 4] Table II summarizes the types, application rates and relative costs of various sinking agents.

The most prominent large-scale application of sinking agents was that undertaken by the French to sink large masses of *Torrey Canyon* oils in the Bay of Biscay. Some 3,000 tons of calcium carbonate, (blackboard chalk from the Champagne area of France) coated with about one-per cent sodium stearate, was used to treat and sink about 20,000 tons of floating oils, although this amount was never precisely defined. The powdery chalk was sprayed or sprinkled over the thick, highly viscous and weathered oil patches and thereafter the water surface was mixed by vessels criss-crossing the area. The oil-chalk mixture reportedly sank in about 60-70 fathoms of water. The area of sinking was known to partially cover scamp fishing grounds and thus there was fear of bottom inundation and oil resurfacing. Numerous observations, since this incident, however, have reported no adverse effects upon fisheries and bottom life, and there have been no sightings of resurfacing oils upon the water or adjoining shorelines. Nevertheless, it was concluded that lack of knowledge on the precise fate of the oil shows need for further trials before this method may be recommended in other situations.[15, 16, 17]

Opinion still remains divided on the use of oil sinkants as to their efficiency, cost, application, and possible adverse effects. With sinking agents, the same problems are encountered in the application and distribution as was indicated with floating sorbents. However, with sinking agents, operational logistics become increasingly more difficult because of the much larger amounts of material required for treatment.

Although damaging effects have been ascribed to toxicity and smothering of bottom life by sunken oils, the sinking approach serves to localize oil pollution, to prevent its spread over the water surface, and theoretically submerge and anchor the oil near the source of pollution. Considering that the bottom of harbors and bays near many industrial ports are grossly polluted and nonproductive, emergency sinking of oils in these areas may not increase damage to fisheries. Dilution by flowing waters in certain areas may also be sufficient to adequately minimize toxicity to nearby shellfish grounds. The other important point of view is that sinking agents, even if used in harbor areas because of fire or explosion danger, can at best be of temporary benefit. The resurfacing oils, although less objectionable due to weathering, may require pick up. Furthermore, sinking may greatly extend the period over which aquatic fauna and flora are affected.[1, 2, 8, 12]

Oil Gelling Agents. These are applied over the surface or periphery of a floating oil slick and are intended to absorb, congeal, entrap, fix, or make the oil mass more rigid or viscous so as to facilitate subsequent physical or mechanical pick up. The gelling concept is also undergoing extensive study for stabilizing petroleum cargoes aboard a stranded or heavily-damaged tanker at sea subject to mass spillage.

Possible gel agents include molten wax or soap solutions, lanolin, liquid solutions of natural fatty acids, soaps of the alkaline metals, treated colloidal silicas, the amine-isocyanatates, and the polymer systems. One manufacturer indicates a cost of $3 per gallon of gel agent, a use ratio of about 1:1, and the ability to mix the recovered gel mass with fuel oils serving as replacement bunker fuel. This gel agent is applied to the surface of the water by a high-pressure spray system to provide sufficient agitation and mixing of the gel-oil mass.

Preliminary research on the gelling of tanker cargoes tends to show that a 3-10 per cent gel agent will be required at a materials cost of 13-40 cents per gallon of tanker crude oil gelled. However, total operational costs, and the ability to salvage and reuse the gelled cargoes, are not fully known at this time.

The gelling approach for treating oils on water, although promising, must provide greater attention to application and distribution, lower materials and operational costs, and suitable means of picking up the amorphous oily masses. Bunker C, heavy crude oils, and some gel agents by themselves may clog intakes, pumps and suction lines. The major difficulty is the ability to harvest the congealed mixtures since gelled oils cannot be easily collected by mechanical or manual means. Necessary improvements are needed in the gelling approach in line with a total operational systems cleanup.[1, 2, 3, 8]

Oil Burning Agents. These were likely considered when the *Torrey Canyon* was in the final stages of destruction off the British coast in March of 1967. As a last resort, the British Government attempted simultaneous and complete burning of the 15,000–20,000 tons of oil remaining in the badly-broken tanker by aerial bombing, incendiaries, and catalyst-oxidizing devices. The major objective was to penetrate and lay-open the decks by "explosive surgery," exposing the oil in the storage compartments to large amounts of oxygen required for burning. High-explosive, 1,000-pound bombs filled with aluminum particles, thousands of gallons of aviation fuel, napalm bombs, rockets, and sodium chlorate devices served to produce a massive fire, if not a sustained fire. The British concluded that no appreciable amounts of oil escaped burning, but if any did, it was lost to the open sea.[13, 14, 18]

Burning of oil by special methods and materials seems to offer an attractive and perhaps inexpensive means of eliminating large amounts of oil over a water surface, providing of course, the many significant hazards are also recognized. Freshly-spilled oils and crudes containing volatile components are relatively ignitible. If a thick layer of oil on water is present, the oil will sustain burning until the volatiles and a portion of the heavier fractions are combusted. Conversely, with fresh oil spills within a harbor or confined area, a significant fire danger exists when the level of hydrocarbon vapors is within the range of flammability, (e.g., gasoline, aviation fuels, or light crude oils).[2, 8, 19]

Wood, debris or other material caught within an oil slick can serve as a wick to start or sustain an oil fire. The cooling of a layer of oil by the water body beneath will greatly deter burning. However, the wick will withdraw the oil and insulate the burning oils from the cooling action of the water, and at the same time provide a renewal and vaporization surface for combustion.

Experience by certain investigators has indicated that floating oils on the sea with thicknesses less than 3 millimeters (0.12 inches) will not burn. It is also reported that layers of kerosene, gas oil, lubricating oil and fuel oil on water will not burn at all without a wick. In one instance, attempts were made to ignite fresh Iranian crude oil five minutes after a spill without success. Once an oil spillage has spread, the material quickly loses its volatile components and ignition is extremely difficult. Weathered oils are consequently reported to present almost no fire hazard.[2, 3, 8, 19]

Commercial burning agents are available for promoting combustion of an oil slick. However, in most cases it is apparent these agents are designed for a relatively thick oil layer which is sufficiently contained. These agents are intended to serve one or more functions such as providing increased surface area exposed to burning; addition of catalysts, oxidizers and low-boiling volatile components; absorbence and entrapment of the oil; or creating a wicking mechanism via surface diffusion and capillary action by the material added.

In experiments carried out by FWPCA at its Edison Laboratory, a heavy fuel oil and a light-weight crude oil were placed atop a layer of water contained in metal tanks with 24 square-feet of exposed surface area. Attempts were made to combust the oils using different burning agents. It was concluded from these experiments that the light crude, freshly applied in a floating thickness of 2.5 millimeters (0.1 inches), required external support with burning agents and an ignition source to burn near completion.

When the No. 6 fuel was used for testing, one of the agents used would not sustain burning at a thickness of 1/2 to 2/3 inches. Another agent generously applied over the surface of the No. 6 fuel cuased sporadic burning and the minimum required oil thickness to sustain burning was 1/3 to 1/2 inches. It is important to note that a thickness of 1/3 to 1/2 inches is equivalent to an oil slick of 7 million gallons/sq. mile. It was evident after this burning that appreciable oil was still remaining. A third agent used performed well with the No. 6 fuel at a thickness of 1/10 to 1/4 inches. The manufacturer producing this material, however, suggests that in order to have complete burning of all the oil, the oil layer must be completely covered with the material with no broken patches. Required amounts of this material (very-low bulk density) may be as high as one pound for each 12–15 square-feet of oil slick.[1, 3]

Oil slick burning experiments with or without special agents as far as is known, have not as yet been undertaken in large-scale in this country; however, the United States Navy is planning a program during the Spring of 1970. Factors of logistics, application, possible recovery of residue, direct or indirect toxicity and damage to aquatic life resources, costs, and other problems inherent in the real spill situation are not well known. Controlling the burning oil mass and ensuing air pollution problems would appear to preclude intentional burning except where the oil mass is distant from the coastline, offshore facilities, vessels, etc. The safety and welfare of all parties however remote from the burning site are of utmost importance. The possible loss of additional oil, and the loss of a drilling platform or vessel at the source of the spill, must be recognized. Because of potential merits in controlled burning, further research is desired on new methods, techniques and procedures both in the laboratory and in the field, together with additional guidelines for burning.

In summarizing on the use of various chemicals for treating oil spills, a number of factors described in this paper should be carefully borne in mind. Of prime importance is the effect of chemical or oil-chemical mixtures on the water environment. The introduction of certain chemicals into the water or onto the shoreface can destroy the delicate balance of aquatic ecology and result in long-lasting damage or destruction of valuable species intended to be protected by the oil defense measures. Aesthetics may not be the prime consideration. Most effective means for erradicating visible oil may have severe impact upon the water environment compared to far more tedious means of recovering the oil.

The ability of the treatment measures to accomplish the assigned task is another critical factor. Type of oil involved, the physical and chemical nature of the water body, and particular techniques and products used will relate to the effectiveness achieved. The various methods of absorbing oil at the water surface, sinking, gelling, or burning the oil, all have their unique advantages–and disadvantages. First-stage results have been reasonably successful, but each method requires further research and application. Recovery of the oily-sorbent agglomerates likely represents the area of greatest cost and for which new approaches and hardware are seriously lacking at this time. The use of sorbents must be properly visualized as part of the complete operational systems cleanup. For cleaning up a massive oil spill, the total cost of doing business may well range into the millions of dollars.

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The Effluent Society

M.A. Wright
Chairman of the Board
Humble Oil & Refining Company

(Tuesday Luncheon Speaker)

At the outset, I would like to commend the American Petroleum Institute and the Federal Water Pollution Control Administration for sponsoring this open forum for a discussion of oil spills. By bringing together members of government and industry, you have the representation necessary for an objective and comprehensive review of this urgent environmental problem. Through a free and open exchange of ideas as is possible at this meeting, we should all become better informed on the subject and its many problems and become more fully advised as to how it can be resolved.

When I reviewed the program for this meeting, I noted that there were some 30 papers on the topic of oil spills. I quickly concluded that there would be little I could add to this specific subject and, therefore, elected to talk on the related but broader subject of water conservation in general. I would like to give a status report on the nation's progress, at least as I see it, and to suggest some areas where improvement is needed.

In connection with the broader topic of water conservation, first let me say I believe we have made progress, but at the same time we must admit that the battle is far from over. Three years ago, while serving as president of the U.S. Chamber of Commerce, I gave a policy speech on the subject of air and water conservation. At that time, I expressed my concern that business was not fully alert to the problem and indeed was far behind government and the public generally in awareness and in action. I pointed out that business would have to be more responsive; it would have to institute effective control programs and invest heavily in abatement equipment. I also cautioned those who might say they could not afford to do such things, that they could not afford not to.

Fortunately, since that time business has responded. It has accepted a more enlightened role in society. Much of this improvement was a natural reaction to a growing problem; part, however, undoubtedly was encouraged by government policies and programs. Certainly the efforts of the FWPCA and the amendments to the Water Quality Act of 1965 played a significant role in bringing about these improvements. Further, the gain in the number of nongovernment conservation organizations and the increase in activity of those already in the field are indicative of the growing public awareness and concern about the preservation of our natural environment.

But, as mentioned earlier, I believe the record will show that business thus far has done a good job in its conservation effort. Since 1966, business has invested significant amounts in pollution control equipment and research programs, and the level is increasing every year. In 1967, U.S. business spent a little over one billion dollars on abatement equipment. In 1968, such outlays rose 35 percent to \$1.5 billion. For 1969, it is estimated business expenditures will reach close to \$2 billion.

More specifically, for the three years ended in 1968, the petroleum industry invested over one billion dollars on construction, operation and maintenance of air and water quality improvement projects with more than half on water conservation. Included in this, as well, is \$75 million in environmental research. API alone is spending \$3 million annually on research, again a significant part of it on water quality control. As further indication of the petroleum industry's efforts, in 1968, \$222 million was spent for water conservation. This level exceeded the federal appropriations under the construction grant program.

State and local governments have also responded to the task, and all 50 states have instituted control programs under the Water Quality Control Act of 1965. Some states have even established standards for intrastate water resources. Further, some improvements have been made in the control of waste discharge, and thus far over $5.4 billion has been spent by all levels of government, resulting in a marked increase in the number of new sewage treating plants, particularly in recent years.

Thus far, as a nation, we have installed numerous conservation facilities, but perhaps of equal importance, we have also broadened and increased considerably our knowledge of the water pollution problem. We know a great deal more now, for example, about the dangers resulting from excessive use of pesticides and fertilizers, and how such chemicals get into our streams and waterways.

Progress has also been made in conserving our offshore environment. The petroleum industry is now operating under tighter regulations in offshore drilling operations and has made considerable progress in the control of oil spills. And in doing so, the industry has gone beyond government requirements. It has created an insurance fund for the cleanup of oil spills from tanker operations. It has established harbor cooperatives and set up machinery for international cooperation. Recently a group of international oil companies joined together to develop a plan called TOVALOP to insure financial capability to remove oil spilled from tankers through accidents. In the transport of oil, more than three-fourths of the world's crude oil tankers now use a relatively new technique called "load on top" to prevent the discharge of oil ballast water during normal operations.

These accomplishments should indeed be gratifying to all interested in water conservation. But before we become too elated about our contributions to the improvement and well being of mankind, I believe it behooves us to look at the task that is still ahead of us. To return our lakes, streams and rivers to an acceptable level of quality, this nation, according to a report by the FWPCA, will have to spend about $25 billion. Considering the length of time that will be involved and the increase in population expected in future years, undoubtedly this amount will have to be increased considerably. Even now there are those who say we are losing ground.

In tests on projects in the Willamette River in Oregon, waste treatment facilities reduced pollution by 20,000 units, but two plants on the same river were dumping effluents at a rate as high as two million units. Further, in some areas of the country, waste heat from nuclear plants and from factories that use large quantities of water as a coolant are being discharged into our inland and coastal waters. Although this problem may not be as serious as some believe, there is little doubt that it has the potential of becoming significant, and certainly needs intensive study.

Another area that deserves greater attention is the pollution caused by the increasing discharge of solid waste by cities and towns. Every day, about 400,000 tons of solid waste has to be disposed of. Some of it is transformed into smoke and dust and pollutes the air through inadequate incinerators. Some of this waste, however, finds its way into streams and harbors. A troublesome aspect of this problem is that more and more towns and cities are now resorting to burying it. If not done properly, these procedures can contaminate the soil and water resources and result in further impairment of our environment.

But of equal importance, many municipalities lack sewers or adequate sewage treating facilities. I have been much impressed in the National Water Commission hearings in recent months, at the tremendous number of villages and towns throughout the country that have no sewer systems at all. According to one report there are about 30 million people living in areas with no, or inadequate, sewage installations, and it is estimated that about 2,400 communities in the country need to install or improve treating facilities in order to avoid further destruction of the quality of water.

The contamination and pollution of water is not confined to our rivers and lakes; much of this contamination sooner or later finds its way to our coastal areas. Today, the estuaries and wet lands are rapidly becoming obliterated and ruined by the selfishness of man. Only recently has there become some public appreciation of the fact that marshes, tidal flats and other coastal wetlands are not mere wastelands to be casually dredged, polluted or filled. They serve an essential purpose in the ecological chain—in fact, in our own life cycle. According to a U.S. Fish and Wildlife Service tabulation, this country has lost in the past 20 years through dredging or filling alone, over 560,000 acres of estuaries, or about seven percent of the total. This does not include the acres that were lost through man-made pollution and which are just as effectively removed from the necessary ecological process.

These are only a few of the areas that need more attention, but I believe they are sufficient in magnitude and scope to remind us that we are just not getting started. The problem before us is still so great and so important as to raise the question why we haven't made more progress. There are probably many reasons, and I will offer only a few. First, we will have to admit that not all members of society have accepted the fact that air and water quality is a problem of serious proportions; this neglect of social responsibility applies to all levels of governments, as well as to consumers and business. A second factor is lack of sufficient cooperation among the vast array of government agencies at all levels, which at times disagree among themselves and at other times present business and consumers with a baffling set of conflicting rules and regulations. A third possibility is that in efforts to arrive at a workable and understandable criteria for pollution standards, there is a tendency on the part of public officials to lose sight of the problem. The purpose of setting standards is not to get a pollutant down to some arbitrary and meaningless number, but to lower the pollution content to a reasonable and safe level. And fourth, is the lack of funds or the unwillingness to commit the funds that are needed.

On the federal level, the current fiscal restraint, coupled with demands of apparently higher priority programs, have limited the funds available for air and water conservation. But with state and local jurisdictions, the situation is even more serious. Officials at this level not only face the tax revolt that limits the federal government, but they also have increasing difficulty obtaining voter approval of new bond issues. In addition, because of inflation, many projects are being reduced or eliminated because current costs exceed the amounts available. Without the necessary funds, these governmental jurisdictions cannot achieve their own goals, let alone those that society seems to be demanding.

It is obvious that there are many obstacles to be faced if we are to have clean air and water. But it is equally obvious that society and technology are moving at a fast pace. Unfortunately, the advance in technology often carries with it the unwanted and adverse side effect of further deterioration in the air we breathe and the water we drink. We will have to accelerate our efforts if we want to catch up. We are now in a pollution revolt, and society is demanding action. Were it not for the Vietnam war and inflation, pollution would be the prime target in the arena of public opinion.

Unfortunately, it is not a problem that can be solved by just one segment of society. All of us contributed to it; it will take all of us to solve it. For consumers and the public at large there will be a cost, both direct and indirect. They must realize that the purity of our air and water will depend on how much they are willing to pay. There will be new regulations preventing the burning of leaves and the littering of the landscape. There will be higher taxes to provide cities and towns with the revenue they need for improved incinerators and treating plants. There will be higher prices for the commodities they buy, so that industry can obtain the funds for abatement equipment.

This cost of conservation should be no different than the cost of conserving our forests. Many years ago, as long as there was no shortage of lumber, it was not necessary to replant trees and recover the costs in higher prices for lumber. Today, however, the cost of replanting, a conservation effort, is included in the price of the finished product. There is no reason why air and water conservation costs should not be similarly treated.

But, governments at all levels must accept their full responsibility. Pollution control is competing with other demands being placed on tax revenues. Priorities must be assigned to these demands, and government officials must be prepared to present their case honestly and effectively so that the taxpayer is in a better position to determine what social goals he wants to achieve and the price he is willing to pay. In dealing with these priorities and goals, sufficient thought must be given to the need of expanding our economic base for future progress. In this era of concern for quality over quantity, we should not lose sight of the fact that material goods are still necessary. We must not allow an economic backlash to eliminate future economic progress. We still need plants, factories, highways and power stations.

In this same vein, government must improve its communication, not only with the general public, but with business as well as with the various levels of governments involved in the war on pollution. In some way, the interested parties must be brought together in a mutual understanding of each others desires and constraints.

For business, there are some who have not yet fully accepted their responsibility. They must be brought into the arena and do their part also. For all of us in business, we must recognize that society has a legitimate concern with its environment, and we must realize that at times there may be more reason for protecting a park or recreation area than in building a plant or installing a marina. In other words, business must accept the same set of rules that apply to others–it must accept a code of social ethics.

But for both business and government, in our planning and implementation, we must accept the fact that we are living in a total environment; we must realize that we cannot solve one pollution problem by shifting the impact to another area–that water, air, solid waste and even noise, are related problems and should not be considered separately. And we must recognize the ecological process and its importance to mankind–in fact, to our very existence. If we disrupt this cycle, we will jeopardize future generations. We cannot substitute man's cycle for that of nature, because if we do, we will not only be letting our effluents jeopardize our affluences, but we will also be jeopardizing the future of mankind.

MECHANICAL HARVESTING

Tuesday, December 16, 2:00 p.m.

Chairman: Ernest Cotton
Air and Water Conservation Advisor
Gulf Oil Corporation

Co-Chairman: B.L. Bragg
Air and Water Conservation Advisor
Standard Oil Company (New Jersey)

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Beach Cleanup

Howard J. Lamp'l
Federal Water Pollution Control Administration
Hudson-Delaware Basins Office, Edison, New Jersey

and

Ralph L. Rhodes
Federal Water Pollution Control Administration
Washington, D.C.

Abstract

The present "state-of-the-art" on cleanup of oil polluted beaches. Examples of past and present beach cleanup techniques. A brief report on present research efforts to remove oil from pollution stained beaches.

Oil, in its proper place, has provided mankind with a myriad of creature comforts and necessities for modern-day living. Oil, on clean white beaches and beautiful shorelines, is uncalled-for and unwanted.

Excluding Alaska, over 60 per cent of the United States Coastline is comprised of sandy beaches. This represents a high potential for recreational use throughout most of its length and is, therefore, highly vulnerable to oil pollution damage.

The present "state-of-the-art" of cleaning beaches of oil is admittedly crude. But, we are learning fast. Every beach or shoreline cleansed of oil pollution adds increased knowledge and technology to the files of our FWPCA, Oil Pollution Research Center at Edison, New Jersey. This information is available to anyone who has a beach clean-up problem.

We are often asked, at the present "state-of-the-art", which is the best method of cleaning an oil polluted beach? The answer to that question is relative. What is the composition of the beach? Is it fine grain sand; is it coarse sand; is it a pebble or shingle beach? What type of oil pollution has fouled the beach? Was it a No. 2 oil, No. 6 oil or a crude oil? How deep is the oil penetration? What is the temperature and the season? Where is the beach located? Does it have access roads? Can it be reached or traversed by wheeled vehicles or can it only accomodate tracked vehicles? Before we can even begin to answer a question on beach cleanup, we have to know as many background facts as there are available.

It has often been said, and I cannot but agree, that nature is the best cleaning agent in the world. This is especially true of rocky shores and stone beaches. If anyone tells you that nature removed oil from a sand beach—dig a little deeper—literally. What nature cannot remove it covers up. Wind blown sand and the seasonal movement of beaches have a tendency to cover up man's mistakes.

The most elementary method of beach cleanup is with the use of rakes, shovels and manpower. If the penetration of the oil into the sand is less than two inches and oil is not too fluid, the oil can be raked into windrows of approximately one foot and picked up with shovels to be placed into a front loader or dump truck. If the oil is not sufficiently weathered to be viscous it can be made more workable through the application of a cold water spray from a garden hose or fire hose.

If the pollution damage to the beach is much more extensive, then mechanical equipment must be used. Before allowing mechanical scrapers and bulldozers on the beach, the operators of these vehicles must be cautioned on the amount of beach sand to be removed. Blades on this type of equipment should be lowered only to the extent necessary to remove the deepest penetration of oil.

If the oil is still washing ashore, a series of deep pits can be gouged out of the sand at the waters edge to allow the oil to build up sufficient thickness to permit removal by vacuum tank truck.

Another effective method of protecting a high-use beach from the onslaught of oil pollution is to throw up a

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sand berm approximately three feet high. This can be accomplished with the use of earthmoving equipment or, if necessary, by hand labor. The artificial berm should be placed along the high-water mark, to protect the dry sand above the intertidal zone. If the surf is strong or very active, or if there is an abnormally high tide, the artificial berm will be destroyed. Sufficient to say that the artificial berm will only prove effective in a mild surf and calm weather.

Should sufficient time exist between the notification of an oil spill and its reaching the shore face, one method of alleviating the damage to the beach is the extensive use of straw, either alone, or used in conjunction with commercial "sorbents". Straw, which has a natural absorptive capacity for oil, will absorb between five and ten times its own weight in oil. To be most effective, the straw should be laid along the low-water mark and as the tide and oil move up on the beach, the straw should be worked into the oil, either through natural wave action or by mechanical methods.

We firmly believe that the use of dispersants, emulsifiers and other chemicals is entirely unjustified in the cleanup of oil polluted beaches. In both the *Torrey Canyon* and *Ocean Eagle* incidents, it was noted that the use of chemicals on sand caused the sand to become "quick", making it difficult to walk on and leaving a disagreeable odor in the treated sand. (However, other reports cite this same "quicksand" with oil alone. As the literature on this subject is very vague, further research, by government and private industry, seems indicated.) Mr. L. R. Beynon of the British Petroleum Company, as quoted in the Battelle Memorial Institute Report of November 1967, says, ". . . . and most complaints of the stench of oil on beaches in Cornwall stemmed from the presence of detergent rather than that of the polluting oil".

Dr. Thomas Murphy of the FWPCA, Oil Pollution Research Center at Edison, N.J., did a series of experiments on the penetration of oil in sand in the fall of 1968. The tests were conducted at Sandy Hook, N. J. In his report, Dr. Murphy concluded that various types of persistent oil alone penetrated no more than two inches into the sand, while oil mixed with chemicals (dispersents, emulsifiers, etc.) caused penetration of the mixture into the sand at least three times the depth of untreated oil.

In his treatment of oil-soaked patches of beach, Dr. Murphy reports that with the application of chemicals on the oil and subsequent hosing down of the mixture with sea water, the sand appeared cleansed of oil. However, further investigation revealed that this observation was deceptive, as the oil and chemical mixture was found between four and twelve inches, in irregular bands, below the surface of the sand.

Many attempts have been made to burn oil on the shore face. Through an extensive literature search and personal observations, it is concluded that the burning of oil *in situ* on a contaminated beach is not very practicable. It has been tried with commercial burning agents, flame throwers, "oxygen tiles" and various mixtures of kerosene and gasoline, but all have met with relatively no success. Small, "fresh" pools of neat crudes or light oil can be burned successfully if their lighter ends have not evaporated, but this is a patchy operation at best and is not recommended for cleanup of massive spills.

Sometimes a "high use" beach becomes stained with a light oil such as a No. 2 fuel. This becomes a serious problem because of instant and relatively deep penetration. The only really effective method of cleansing this type of pollution is to expose as much of the contaminated beach sand to the sunlight and wind as possible. This can be done effectively by the use of a harrowing plow or beach cleaning machines, which are used to remove trash from beaches. Number two fuel, in contrast to No. 6 or Bunker "C" fuel oil, contains a relatively high amount of light ends. If these light ends are exposed to evaporation through wind and weather, they will dissipate rather rapidly.

To accelerate the evaporation and dissipation of No. 2 fuel from the beaches, a mat of straw should be laid on the beach, at least one inch thick. A disk-harrow should then be used to work the straw down into the sand column so the straw can absorb as much of the oil as possible. A beach cleaning machine should then be used to retrieve the oilsoaked straw. The beach should then be harrowed or mechanically raked to hasten the dissipation of the remaining oil trapped in the subsurface of the sand.

The Federal Water Pollution Control Administration is presently supporting three projects aimed at improving beach cleanup technology. One is being conducted by URS Systems Corporation to develop more effective and efficient ways to utilize common earthmoving, construction and agricultural equipment in beach restoration operations. In operations involving pickup of oil contaminated beach material for transport to disposal sites, the objective is of course to remove only contaminated material, thus minimizing transportation and handling effort. In the course of the project, URS will investigate: minor modifications to commonly used equipment such as the modification of blades or the addition of baffel wings; changes in procedures such as speed of operation; the use of water or other agents to improve cohesiveness or varying blade angles; and changes in operational approach such as the use of mobile loaders, gravel washers or other equipment in combination with graders and scrapers.

A project being carried out by Aerojet-General Corporation, El Monte, California will determine the feasibility of incinerator systems for restoring oil-contaminated beaches. In principal at least, incineration of the oil at the site has the prime advantages of disposing of the oil on site and greatly reducing handling and disposal problems involved in most present day beach restoration operations. Two basic systems will be evaluated–incineration in place, and incineration in various types of combustion chambers. The most attractive technique–operationally-burning in place–will involve the necessity of heat and oxygen being transmitted some distance under the sand surface to the lower limit of the contaminated sand–a difficult task particularly on wet beaches. An alternate, perhaps a more potentially successful technique would involve picking the sand up and passing it through an incinerator. Two promising incinerator configurations involve a falling curtain of sand contacting a hot gas or a fluidized bed. Fuel requirements and residence time required in the incinerator will be of prime considerations in determining feasibility. Aerojet will submit a preliminary report of its findings later this month.

Another cleaning process is under development by Melpar Incorporated, of Falls Church, Virginia. This project involves the development and demonstration of an adaptation of the froth flotation process to separate oil from contaminated beach sand. The plant will be constructed from readily available off-the-shelf components. Next summer, at an Atlantic Coast beach site, we hope to witness a demonstration of this unit processing a minimum of 30 tons of oil contaminated sand per hour. The design is based on laboratory studies which indicate that the violent agitation in the flotation tank shears the oil from the sand grains, leaving clean sand in the unit underflow and oil and a minimum volume of fine sand particles in the overflow. The clean sand will be returned to the beach and the oil stored for suitable disposal. Major problems to be faced in this project may be the creation of emulsions in the flotation tank and the separation of heavily weathered oil-sand mixtures.

At the present time, we do not have all the answers on beach restoration. But through further research and willing cooperation between government and private industry, the complete and safe removal of oil from our high amenity beaches will be a possibility in the near future.

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Portland Harbor Evaluation

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Abstract

Millions of tons of petroleum products are handled annually through the Port of Portland, Maine. In 1966, a citizens response to a local environmental problem focusing attention on this movement was instrumental in the formation of the Portland Harbor Pollution Abatement Committee, Inc. As a portion of the committee's activities, a study proposal was submitted to the Federal Water Pollution Control Administration which resulted in the award of:

> *R&D Grant No. 150–80–DOZ "Test and Evaluate Mechanical and Pneumatic Barriers to Contain Spilled Oil and Means for Removing the Contained Oil in Harbors and Adjacent Waters."*

The findings from this research and development study will result in the publication of a unique "cookbook" type manual for oil pollution control written specifically for use by the man on the scene at the waterfront.

Controlled testing for this type of research was conducted in what can be considered one of the finest outdoor laboratories. Advanced testing will continue under the same environmental conditions involving the movement of hundreds of both large and small vessels engaged in the transportation and handling of petroleum products. Equipment manufacturers and leading figures working on the problems of oil pollution abatement were drawn to this outdoor laboratory and participated during testing procedures.

Portland, Maine is a major oil receiving port on the East Coast, with the potential of becoming the largest mover of crude oil in the country. In 1968, the Port of Portland handled over 23 million tons of crude, and over three million tons of refined petroleum products.

Portland's strategic position as a major oil port located in an environment attracting summer visitors to off-shore islands, and thousands of boaters to world famous Casco Bay, prompted a group of concerned citizens to organize a committee to learn more about methods to prevent oil spills and to contain and remove them effectively should they occur.

Members of the committee include representatives of the petroleum industry in the area, U. S. Coast Guard, fire departments from the cities of Portland and South Portland, steamship agents, Chamber of Commerce, Maine Port Authority, and civic and business leaders. There are no paid employees, as each member contributes his time and expense.

Funds to purchase boom, necessary auxiliary equipment, insurance and to conduct research were contributed by the local oil terminal operators. Briefly, the program includes the following:

1. Establishment of a communication network to respond to an oil spill immediately with manpower and equipment.
2. Publication of an "Information Booklet on Oil Spills," outlining response and reporting procedures, key personnel, location of equipment and rules and regulations under which the committee functions. Two thousand copies were printed and distributed, mostly upon request from all over the country and from oil ports throughout the world. The booklet has been used by other ports as a guide in organizing oil pollution abatement programs.

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3. Extensive testing procedures to move "containment device" (boom) to the scene. Testing resulted in the design of a catamaran to store and carry the boom and play it out on the scene promptly and effectively.
4. Established procedures to react to a "mystery spill." This created the greatest problem to the committee, when oil appeared on the water in volume, and it was impossible to establish immediate responsibility.
5. Creation of a Data Bank on "oil pollution and abatement problems."
6. Construction of a helicopter pad on the waterfront to insure a more effective communication network to handle manpower maneuvers and to track oil spills in case of a major disaster.
7. The writing of an Oil and Hazardous Materials Contingency Plan for Prevention, Containment and Cleanup for the State of Maine.
8. Incorporation in the State of Maine.

As a result of the work of the Portland Harbor Pollution Abatement Committee, Portland has established a worldwide reputation as a "tough port," and tanker captains everywhere are passing word that, "When you're in Portland, be very careful about spills or you'll find yourself in a lot of trouble."

We acknowledge with thanks the interest, support and cooperation we have received from the petroleum industry, Federal and state agencies and local citizens.

We found during our studies that there appeared to be several weaknesses in the containment, removal and disposal of oil spills. Consequently we applied to the Federal Water Pollution Control Administration for a grant to seek answers that were not readily available. We received $64,350 from FWPCA supplemented by a local "in-kind" contribution in the amount of $36,500.

With funds from the FWPCA Grant and the local "in-kind" contributions, we set up on the local waterfront a laboratory for testing and evaluating oil spill control equipment for this project. The testing area lends itself to controlled* experiments in smooth water conditions and provides for storage and maintenance of equipment and for effective observation and evaluation of testing procedures. Because of its unique design and location, the area gives quick access to rough water testing areas where oil spills can be created and cleaned up within the same environmental atmosphere where millions of tons of petroleum products are handled each year.

The findings from the Federal Water Pollution Control Administration grant will result in the publication of a "cookbook" type manual for oil pollution control written specifically for the use by the man on the scene at the waterfront.

It will contain detailed descriptions of the basic equipment designs available, their operating characteristics, and practical limitations in use. Details will be provided on handling, rigging, storage procedures, and other data related to field experience. This will provide a basis for determining how a piece of equipment can best be used to fill an individual's particular needs. Ease of equipment handling is considerably different at 2:00 a.m. on a cold winter's night than at 2:00 p.m. on a summer afternoon.

The data gathered in preparing this "cookbook" manual will be included in our *final report* to FWPCA. It will be of value to the engineer in further analyzing equipment characteristics and useful to the manufacturers in modifying existing equipment and developing new designs. Detailed descriptions of the sampling and analysis techniques, and equipment used, will also be included in the hope that they will find application in other areas.

The purpose of this project, as defined in the contract, is to "test and evaluate oil booms and a diffused air curtain bubble barrier for oil spillage containment and the design, construction and evaluation of oil recovery devices to remove the contained oil from the waters". Oil recovery includes the ultimate disposal of reclaimed oil and of sludge residues.

In approaching this assignment, it was immediately evident that there were no industry standards against which to judge the equipment and there were no objectives or specifications for the design of any new equipment which might be needed.

Consequently, initial efforts at organizing the project were directed to an understanding of the "anatomy" of an oil spill; the part which equipment might play in combating each stage of that spill, and the development of standards which such equipment should meet, together with optimum methods for operating such equipment.

In the final report to FWPCA, we will specify equipment requirements and operating characteristics for a complete system for oil spill containment, removal and disposal. Needs for the development of new equipment will be detailed. Work to date has provided a substantial portion of this information and details will be forthcoming. In carrying out our approach to the project, we have assembled 50 pages of data on tests, supported by a library of over 300 colored slides and over 30 Polaroid color shots.

We have established a working relationship with more than 20 suppliers of materials and equipment. We have worked with equipment supplied from Norway and Switzerland and from all sections of the United States. We have spent the time needed to learn to use that equipment as directed by their personnel. We are most appreciative of the information received from the suppliers, and sincerely trust that our evaluation of that equipment will benefit their continuing efforts to supply satisfactory designs to meet the needs of this international market.

Material furnished by equipment suppliers and other agencies has expanded into a voluminous file of information which is available to Government and will be made available to private industry for further research.

The "smooth-water" phase of the project has been completed, and evaluations are nearing completion on several types of equipment.

Mechanical Barriers

We have completed smooth water testing on six different mechanical barriers having drafts of 18 inches to 24 inches and freeboard of 12 inches. All of these mechanical barriers can be useful under some conditions. We have tested them for their ability to contain oil and to counteract the forces which act on an oil spill as a result of wind, wave or other conditions.

In testing each barrier, we used a standard towing technique wherein oil was spilled into a loop of the barrier during forward movement at the rate of 1 K to 3 K's. This test enabled us to evaluate the ability of the barrier to divert oil into the vee of the loop and to contain the oil in that position at varying speeds. Skimmers were operated in the vee of the loop to remove the oil thus contained.

In general, the "fence" type barriers with their high freeboard and rigid sub-surface structure showed promise of containing oil under some severity of wind and wave action, while the "curtain" type barriers were more successful in smooth water and under limited wave action conditions.

It became apparent that oil could be contained and could actually be moved around on the surface of the ocean at very slow relative speeds. In our test configuration, the "curtain" barriers could contain oil at relative speeds of less than 1 K and the "fence" type barriers could contain oil at speeds of approximately 1½ K's. Several suggestions for improvements were relayed to manufacturers and in some cases these have resulted in design changes or in new design concept.

There appear to be problems in the design of towing hitches and connectors which join one section of equipment with another. In one instance, wave action loosened connector bolts on one design of the towing hitch. In another case, hose couplings corroded after protracted exposure to the elements and created serious delays in the assembly of hoses between skimmers and pumps. These weaknesses were relayed to the manufacturers and steps have been taken by them to modify or re-design as necessary.

We found that the connector plate supplied by one manufacturer was not compatible with a boom designed by another manufacturer and we had to design and build our own connectors whenever we wanted to join two different booms end to end. We strongly recommend that an industry committee be formed to work out a universal design for joining one boom to another of different make just as fire hoses are equipped with universal couplings.

In another instance we found that loose cables and lines create tangling problems during the deployment of some mechanical barriers. Steps are already being taken to remedy this annoyance.

In all instances where a boom was immersed in salt water for a long period of time, we encountered substantial quantities of marine growth on sub-surface sections. In permanent installations, this will create problems and hazards. We suggest to industry that measures should be taken to combat marine growth or to provide for easy and effective means for periodic removal of such growth.

It is obvious that barrier design will change substantially in the next few years and there are many areas where barrier performance could be improved both in the containment of oil in rough water conditions and in their ability to function effectively as part of a complete system, including work boats, pumps, skimmers and storage and removal equipment.

Air Barriers

We have tested air barriers at depths from 2 feet to 30 feet. Barriers have been suspended from floats and placed on the bottom.

The air barrier we tested was of local manufacture and is limited to 120 cubic feet a minute and 100 PSI in pressure. Nevertheless, it showed considerable ability to contain or divert thin oil spills driven by wind or moderate tide currents. This type of equipment has potential for many applications in fixed locations. We have also determined that it can be highly mobile, can be easily transported to the site of a spill and deployed for diversion, containment or protective purposes.

Hose for air barriers is relatively inexpensive, the equipment is easy to store and handle and we suggest that attention be given by the industry to designing and marketing this type of equipment so that it can be used to protect marinas, lobster cars and other sensitive areas in smaller communities. In the design, attention must be given to providing an inexpensive but functional air compressor that might be interchangeable with other productive work within the area or community.

Skimmers

The development of skimmers requires a major continuing effort. We consider this to be the most important single design problem in the project.

We have had our best success to date with a circular weir skimmer of foreign manufacture and feel that this design holds potential for further development.

In addition, we have experimented with a high volume rough water skimmer which shows some promise in its ability to conform to wave action, but it is too early to go beyond the point of cautious optimism in our evaluation of this model.

Pumps and other accessories used with skimmers need to have these features incorporated in their designs.

1. Dependability—carburetors, magnetos, points and plugs need to be protected against ocean air and salt spray.
2. Portability—easy to transport. Equipment must have good balance and good handles for manual lifting, and sling attachments for mechanical hoisting.
3. Quick and positive coupling and uncoupling of hoses and other connections is essential.
4. Low maintenance costs and easy cleaning and storage arrangements.
5. Ability to work in gangs to handle increased volumes.
6. Protection from clogging due to seaweed or other debris.

Storage and Separating Tanks

Early in this program we encountered the need for a floating tank having enough capacity for the storing, transporting and separating of large volumes of an oil/water mix.

Through the FWPCA we obtained a fabric tank of 5,000 gallons capacity and have found it very useful for that purpose. However, it was not designed for marine use, so we equipped this tank with auxiliary flotation, inlet hoses, discharge hoses and an air vent so that it could be used with our skimmer pumps and transfer pump equipment. The result has been highly successful. The tank serves as primary storage to receive the oil/water mix from the skimmers, and, when time permits, it serves as a gravity separator. It is easy to tow as a transport vehicle to deliver its contents to a shore-based separation system.

It is our conviction that floating tanks of this general type will be useful in several applications and in capacities of much greater volume. We might make note here that attention should be given to the design, manufacture and installation of an effective shore-based separation system.

Instrumentation and Sampling

Our group has made use of basic weather instruments to measure wind speed, direction, temperature, humidity, and barometric pressure during our testing program. Various types of photography have been used to record tests. This includes infrared photographic equipment and other advanced photographic techniques both on the surface and under the water.

We have used sensitive marine speedometers to measure surface and sub-surface currents and we have developed simple inexpensive techniques for extracting core samples of spill tests for chemical and physical analysis.

Compatibility of Equipment

In testing the types of equipment previously described, we are aware that each unit must be compatible with other units to form a complete system. For example, it should be possible to join two or three different designs of mechanical barriers end-to-end when greater length is required. It should also be possible to attach barriers to skimming equipment so that no loss of oil takes place at the joint. The discharge from skimmers must be piped into floating tanks and those in turn must be effective as units of a separating system. It is our conclusion that industry is rapidly developing an awareness of this requirement for system operation and that future designs will give far more attention to the need for meeting this requirement.

Conclusion

We are very pleased to have this opportunity to produce one of the first published reference documents dealing with a system approach to cleaning up oil spills. Further, the "cookbook" section of the report will be unique in that it will be written for use by the men on the waterfront who deal with these problems most frequently.

There is available within the report information that will be of value both to the engineer in evaluating the different equipment capabilities, and that, hopefully, will also provide the manufacturers with a basis for improved design.

The study has been very revealing to the Maine Port Authority and the Portland Harbor Pollution Abatement Committee and after the release of the final report, we hope it will be equally as useful to the rest of the country.

Study Of Equipment And Methods For Removing Oil From Harbor Waters

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Abstract

A cost effectiveness analysis was performed for equipment, materials, and techniques for the removal of spilled petroleum products from the surface of port and harbor waters used by U. S. Naval craft. Effectiveness criteria, formulated for present methods and presently available equipment and materials, included speed of application, completeness of removal, ease of operation, effect on marine life, operating continuity, and availability. Parameters for the effectiveness study were based on the petroleum products now in use or those planned for future use and a detailed review of the geographic, hydrographic, physical, and environmental characteristics of ports used by the U. S. Navy. The two most cost-effective systems for broad application were found to be mechanical recovery of spilled material by surface suction devices, supplemented by mechanical containment, and the application of chemical dispersants by pier- or vessel-mounted high pressure spray equipment.

Many types of equipment, materials, and techniques have been employed to remove spilled petroleum products from the surface of harbor waters. The range of credible spill situations and petroleum products associated with Naval craft suggests that no single system is likely to be completely effective. This study was performed to identify and describe the most cost-effective available systems consisting of present or new combinations of existing equipment, materials, and techniques. Deficiencies and specific measures for future employment by the Navy were to be identified for the combat of spills at Naval installations in port and harbors in consideration of costs, effectiveness, speed, hazards, ecological effects, environmental and geographic factors, and physical features of the port or harbor. The study focused on the major petroleum products in current use by the Navy or planned for future use. The study was performed under contract N62399-69-C-0028 to the U. S. Navy.

A rational decision-making methodology was developed for choosing among alternative countermeasures against petroleum product spills from Naval craft in ports and harbors. The study encompassed detailed analysis of the effects and behavior of spilled oil, state-of-art study of available materials and methods, and detailed review of Navy methods and experience in dealing with oil spills, as well as the development of the decision-making methodology. This presentation will be confined to the latter aspect to illustrate the methodology developed with the expectation that it may be successfully applied to several aspects of the oil pollution problem.

The principal ingredient of the decision-making methodology is an effectiveness analysis.

Effectiveness Analysis

Systematic analysis of the effectiveness of systems for removal of petroleum product spills from port and harbor water surfaces requires assessment of specific operational aspects under a range of conditions. These conditions are parameters whose extremes are the boundaries for the assessment.

"Effectiveness" is not quantifiable unless specific characteristics which contribute to or detract from the overall effectiveness are considered. The identification of such characteristics, criteria for judging them, and a rational plan for combining them into overall effectiveness are presented in the following paragraphs.

Effectiveness Criteria

The criteria for the effectiveness measurement should minimize the subjective judgment which must be employed. Rather than attempt to finely rank each system with respect to the criteria, which would inject undesirable subjective judgment into the analysis, we chose to establish the individual criterion in terms of minimal performance requirements. Each system is then given a numerical index which reflects whether it exceeds, meets, or fails to meet each of the criteria. The sums of these indices, for all combinations of parameters, then reflects the overall relative effectiveness of a particular system.

The effectiveness criteria employed in this study are listed in Table 1. The rationale for their development is given in succeeding paragraphs.

Completeness of Oil Removal. One of the important performance characteristics of a petroleum product spill removal system is the degree to which it can approach complete removal of the petroleum product from the water surface. Systems which are less than perfect may be adequate if the fraction removed is sufficient to effectively mitigate the effects of the spill–property damage, destruction of marine life, and damage to recreational resources. This would be the case if the residual material remaining on the surface can be harmlessly removed by natural mechanisms. Also, it requires that chemically dispersed materials do not reappear at the surface at a later time.

Among the factors which relate to the degree of completeness required of a spill countermeasure are:

1. Potential property damage due to residual material–depends on characteristic of petroleum product
2. Potential damage to marine life due to residual–depends on characteristic of petroleum product
3. Size of spill
4. Frequency of spillage
5. Winds and currents at spill locale

This study is concerned with relatively small spills of specific petroleum derivatives–Bunker C, Navy Special, JP-5, and Distillate Fuel.

Information on rates of natural degradation (bacterial action, oxidation, and dissolution) is limited to certain crude oils and to very specific environmental conditions. It is not possible to extrapolate these data to the diverse parameters of concern in this study.

In reality, any system worthy of consideration must be theoretically capable of essentially completely removing the offending product from the water surface. Some systems, especially mechanical ones, cannot be expected to do this under certain adverse combinations of environmental, geographic, or hydrographic parameters considered in this study.

TABLE 1. EFFECTIVENESS CRITERIA

Operational Aspect	Criteria
Completeness of Removal	Essentially complete removal in consideration of environmental, geographic, and hydrographic parameters.
Speed of Application	Recovery at a rate such that removal from surface waters is complete before a slick causes damage or before it spreads so thin that it cannot be effectively treated. Includes deployability and mobility considerations.
Does Not Increase Pollution or Hazard	Must not introduce materials having greater propensity for property or recreational resource damage than the contaminating petroleum product. Primarily applicable to chemical or chemomechanical methods.
Applicability to Limited Access Areas	Must be capable of operation among piers, berthed ships, pilings, and structures which limit access. Primarily applicable to spills in berthing areas. Judgment based on maneuverability and size.
Sensitivity to Natural Phenomena or Floating Debris	Must be capable of operating under the anticipated sea, wind and current conditions prevailing at spill scenes 90 per cent of the time. Must not be rendered inoperable by minor floating debris, or where applicable, by water-in-oil emulsions. Primarily applicable to open area spills.
Toxicity to Marine Life	Will not contaminate fisheries and other commercially or recreationally significant marine life to cause mortality, condemnation of fish products, or flavor degradation.
Availability	Will be available for application at least 95 per cent of the time in consideration of reliability and repairability of candidate systems.

Each system will be evaluated for the combinations of parameters involved in this study, by considering its design features which detract from or contribute to the completeness of petroleum product removal. Those which are capable of providing essentially complete removal will be given an index of (+1) and those which have severe limitations in this regard will be given an index of (-1). Those which appear theoretically capable of complete removal performance, but are undemonstrated for the particular combination of parameters involved, will be given an index of (0).

Speed of Applications. A measure of the effectiveness of an oil spill countermeasure is its ability to contain or remove the offending material before it damages vulnerable property or marine life. Oily materials generally spread, or decrease in thickness, with time after spillage, and removal must also be effected before a slick becomes so thin that it is untreatable or unrecoverable.

Where the wind conditions are calm and currents are not significant, the rate of movement of the edge of a

TABLE 2. THEORETICAL SLICK DIMENSIONS AFTER SPILL

$$\text{(Diameter of Slick)}^3 = \frac{24}{\pi} K(d_w - d_o) \frac{d_o}{d_w} V_o t + D_o^3$$

		200 Gallon Spill		2,000 Gallon Spill	
	Time After Spill	Thickness, Inches	Area Thousands of feet^2	Thickness, Inches	Area Thousands of feet^2
Navy Special	10 min	0.0502	6.4	0.113	28.4
	1 hr	0.0155	20.7	0.034	94.7
	2 hr	0.0099	32.5	0.022	149.5
	5 hr	0.0054	59.5	0.012	277.0
	10 hr	0.0039	94.7	0.0073	439.0
JP-5 and Distillate Fuel	10 min	0.0135	23.7	0.0293	109.8
	1 hr	0.0041	77.9	0.0089	362.0
	2 hr	0.0026	123.7	0.0057	576.0
	5 hr	0.0014	227.0	0.0030	1,060.0
	10 hr	0.0009	362.0	0.0019	1,682.0

slick will be controlled by the spreading rate. No directly applicable quantitative data on spreading rates for the materials of concern (JP-5, Navy Special, Bunker C, and Distillate Fuel) have been found. However, the work of Blokker and Berridge, et al,[1] [2] provides some basis for estimation of rates of oil slick spreading. Calculated slick characteristics based on these works are shown on Table 2.

The Blokker equation can be stated as

$$D^3 = \frac{24}{\pi} K(d_w - d_o) \frac{d_o}{d_w} V_o t + D_o^3 \qquad (1)$$

where

D = slick diameter, meters

d_w, d_o = density of water and oil, respectively

V_o = volume of oil, cubic meters

t = time after spillage, minutes

D_o = slick diameter at $t = o$

K = a constant depending on the oil

Since the driving force for spreading is proportional to the difference in density between the water and oil, and the density of Bunker C is very near that of sea water, the Bunker C will have little or no tendency to spread. In addition, the pour point of Bunker C will usually be above the temperature of the sea water. This will further inhibit spreading.

Values of K for the petroleum products of interest in this study have not been determined. However, Blokker has determined this constant for several refined products, some of which resemble JP-5, Navy Special, and Distillate Fuel. The JP-5 and Distillate Fuel have similar densities and viscosities and closely correspond to Blokker's gas oil (Sp. Gr. = 0.83, $\mu = 4.3$ cP at 20°C). Navy Special is similar to the lubricating oil tested (Sp. Gr. = 0.90, μ = 490 cP at 20°C). The values of K, for these materials, were 15,000 min^{-1} and 9800 min^{-1}, respectively, and were used herein. It should be noted that the K value is either insensitive to viscosity or viscosity effects are masked by surface and interfacial tension variations. Furthermore, since the diameter of an oil slick at a given time is proportional to $K^{1/3}$, a K which was 50 per cent too large would result in only a 15 per cent error in the calculated diameter.

There are two other factors concerning the rate of spreading of an oil slick which are pertinent to this study. The first is that the initial rate of spreading, immediately following the failure of the oil container, is assumed analogous to the sudden failure of a dam. The potential energy of a thick oil layer is essentially converted into kinetic energy and the effects of viscosity, evaporation, surface tension, and interfacial tension are negligible during this first phase. Blokker found that this first phase continued until the slick thickness had reduced to about 2 cm. From this point on, he found that 90 per cent or more of the potential energy was dissipated in overcoming friction. The first phase requires on the order of one minute for a 100 m^3 (26,400 gal) spill. Thus the area covered by a spill of 200 gallons would equal 407 ft.^{2} in less than one minute, and by a 2000 gallon spill, 4070 ft^2. After the oil slick had reduced to this thickness, the

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[1] Superior numbers refer to literature references at conclusion of text.

TABLE 3. MINIMUM SPEED OF APPLICATION CRITERION FOR GOVERNING PARAMETERS

Parameters					
Location of Spill	Petroleum P Product	Spill Size, gal	Type of System	Minimum Treatment Rate	Basis
(1) In proximity to piers and berthing areas where access is limited by pilings, enclosed areas, floats or booms.	JP-5 and Distillate Fuel	200	Mechanical	735 ft^2/min	Minimum film thickness treatable. Treatment within a fixed time span
			Chemical	735	
		2000	Mechanical	3400	
			Chemical	3400	
	Navy Special	200	Mechanical	550	
			Chemical	550	
		2000	Mechanical	2450	
			Chemical	2450	
	Bunker C	200	Mechanical	0.67 gal/min	
			Chemical	0.67	
		2000	Mechanical	6.7	
			Chemical	6.7	
(2) Readily accessible open areas of bays and sounds when environmental conditions are moderately severs; (assume wind 20 mph on shore, and spill 1-1/2 mile off-shore).	JP-5 and Distillate Fuel	200	Mechanical	790 ft^2/min	Recovery before oil reaches shore'. 1/2 hr for deployment and slick movement at 4% of wind velocity assumed.
			Chemical	790	
		2000	Mechanical	3650	
			Chemical	3650	
	Navy Special	200	Mechanical	590	
			Chemical	590	
		2000	Mechanical	2700	
			Chemical	2700	
	Bunker C	200	Mechanical	2.4 gal/min	
			Chemical	2.4	
		2000	Mechanical	24	
			Chemical	24	

Blokker relationship would apply and the rate of spreading for JP-5, Distillate Fuel, or Navy Special can be estimated from the ranges of values given in Table 2.

The second factor of importance is that, as shown by Berridge, the thickness of a slick, after the lapse of a full day, tends to approach the same value (0.0008 to 0.0012 in. in their reported tests) for a group of oils covering a wide range of properties. It is probable that the JP-5, Distillate Fuel, and Navy Special would all exhibit this characteristic.

At some point in time, the effects which compete with the spreading force will become controlling. These are evaporation with the attendant density and viscosity changes, and the formation of water-in-oil emulsions. Evaporation, particularly, can become a very important factor for products having high vapor pressure constituents. Blokker found that up to 80 per cent of a gasoline slick evaporated in three hours under moderate wind conditions. In the cases of interest in this study, evaporation is less important—but still causes the theoretical slick dimensions to be conservatively large.

Under ideal conditions, with surface active components, films on the order of 4 x 10^{-5} inch thick have been observed to form after 40 to 100 hours. Blokker also found, however, a final film thickness of 150 microns for gas oil on uncontaminated water. This material is most representative of the materials considered in this study, and this thickness is a reasonable minimum film thickness for effective operation of most mechanical removal systems.

The required recovery rate, within the previous context, revolves about the ability of a system to treat a given water surface area within a specified time span. Effectiveness criterion is best expressed for rapidly spreading materials as area treated per unit time. For slowly spreading materials such as Bunker C, the required recovery rate is best expressed as volume treated per unit time.

It is apparent that the required treatment rate will be a function of the characteristics of the oil derivative involved, the size of spill, the location of spill, and the type of recovery system involved.

The material requiring most rapid treatment, on the basis of spread rates, is JP-5, followed by Distillate Fuel, Navy Special, and Bunker C, in that order. For Bunker C, where little or no spreading tendency exists, the required treatment rate would be governed by other factors such as the need for operation during daylight hours or the need for recovery before winds or currents carry the material to vulnerable property or marine life.

For all treatment methods, deployment speed becomes an important consideration for rapidly spreading oil slicks.

Criteria for all methods whose removal efficiencies are not sensitive to film thickness may be governed by the ability to visually locate a spill slick. For spills close to docks, sufficient illumination is assumed to be available for location and treatment. However, for spills in a bay or sound, effective treatment could only be undertaken during daylight hours. For such cases, it is arbitrarily assumed that at least five hours of daylight would be available for countermeasure application in the vast majority of cases.

For some postulated spill cases, onshore currents and winds may become controlling.

It follows from the above discussion that different quantitative recover rates are required for each combination of parameters. For purposes of this study, and on the basis of the above reasoning, criteria were selected for various combinations of parameters. These are shown on Table 3.

It should be recognized that these detailed criteria apply to systems which do not utilize booms or other containment devices to prevent free wind-driven or spreading movement of the offending material.

For purpose of comparing various systems, the following indices will be utilized in the total effectiveness:

System Condition	Index
System exceeds criteria	+1
System meets criteria	0
System fails to meet criteria	-1

Effect of Method on Pollution and Hazard. Generally, mechanical methods of spill treatment do not cause adverse effects. An exception to this would be mechanical systems which involve containment by booms or corrals when employed on spills of JP-5. If chemical dispersants were not applied to minimize the fire hazard, prevention of spreading of this flammable material, by gathering it in such containment, might be undesirable because of the associated fire hazard.

Chemical methods must be carefully considered because of the possibility that the chemical may be more harmful than the petroleum product. Chemical materials that would degrade structures, accelerate corrosion, or otherwise attack submerge cables, pipelines, or water craft are of particular concern. Also, the possibility of the dispersed material reappearing at a later time must be considered.

The index to be applied will be as follows:

Effect	Index
Reduces Pollution or Hazard	+1
No Effect on Pollution or Hazard	0
Increases Pollution or Hazard	-1

All cases based on specific combinations of parameters and for particular systems will be individually considered and indexed as indicated.

Applicability to Areas Having Limited Access. A typical port installation includes piers supported by pilings, breakwaters having irregular geometry or porous characteristics, berthed ships, and various irregular fixed or floating objects. The presence of these kinds of objects can make a countermeasure system, which is eminently satisfactory on the open water, totally ineffective.

Consideration of this aspect, in the effectiveness analysis, will consist of evaluating each component of all hypothetical and actual systems in terms of:

1. Access requirements in terms of water surface area and height and width of width of planes perpendicular to water surface needed for effective application.

TABLE 4. CALCULATED WAVE HEIGHT FOR 90 PER CENT PROBABILITY

Port Area	Maximum Wind Velocity Expected 90% of Time, mph	Prevailing Wind Direction	Fetch, mi	Average Water Depth, ft.	Maximum Wave Height, ft.	Average Wave Length, ft.	Minimum Wave Length, ft.
Puget Sound	≤18	SSW	3.0	130	1.4	24	8
Long Beach	≤9	W	0.8	45	0.4	8	3
San Francisco	≤20	WNW	5.0	60	1.6	31	11
San Diego	≤11	WNW	2.0	30	0.6	13	4
Boston	≤21	SW	0.5	35	0.8	15	5
Charleston	≤16	NE	0.8	38	0.6	12	4
Norfolk	≤18	SW	2.0	41	1.1	21	7
Hawaii	≤20	ENE	2.5	40	1.4	26	1

2. Maneuverability of system in terms of turning radius and reversability.
3. Stability if floating or fixed objects are struck during movement.

Each system will be individually evaluated for the parametric situations involving the obstructions mentioned above. Indices will be assigned for each system and parametric case as follows:

Applicability to Limited Access Areas	Index
Exceeds Needs	+1
Meets Needs	0
Does Not Meet Needs	-1

Sensitivity to Natural Phenomena or Floating Debris. Many mechanical systems are susceptible to stalling from pluggage or blockage by floating debris. It is usual, in port installations, for variable amounts of debris such as driftwood, paper, etc. to be present on the water surface. Those systems involving suction pumps, weirs, and close tolerance impellors are examples of systems which may be adversely affected by such materials. Design features such as screens, strainers, and baffles may enable a system to effectively handle such floating debris.

Systems employing rotating drums or endless belts of sorptive material are vulnerable to damage and stalling if rigid debris with sharp corners is picked up at the water surface. This characteristic may be contrary to some manufacturers' claims, but is has been observed during field application.

The sensitivity of a hypothetical or actual system to water wave and wind conditions is a significant performance factor. While it is unlikely that spillage would be of priority concern during severe storm conditions, effective systems must be usable during conditions more severe than "flat calm." "Harbors" implies some degree of protection to ships and facilities from conditions which might prevail on the open sea. Man-made breakwaters, spits, and jettys and the natural geography provide this protection. It seems appropriate, for purposes of this study, to select conditions which would prevail during the vast majority of the time—more severe than "flat calm" but less severe than open sea storm conditions.

U. S. Navy installations having the greatest past spillage problem and the greatest general propensity for future incidents are Puget Sound, Long Beach, San Francisco, San Diego, Boston, Charleston, Norfolk, Newport, and Hawaii. Wind distribution data along with the calculated short period wave height calculated from fetch and water depth, based on the method of Bretschneider,[3] for these locations are given in Table 4.

As can be seen from this table, the maximum normal wave height varies from 0.6 to 1.6 ft. For purposes of this study, the maximum wave height during spill countermeasure operations will be taken as 1.6 ft.

The indices to be applied to this aspect of countermeasure effectiveness are as follows:

TABLE 5. COST SUMMARY

SYSTEM	SITUATION A Cost Per Incident	SITUATION A Cost Per Gallon	SITUATION B Cost Per Incident	SITUATION B Cost Per Gallon
1. Sorbents/Manual Retrieval Plus Containment	$1,060	$2.65	$1,060	$1.60
2. Gellants/Manual Retrieval Plus Containment	2,000	5.00	2,600	3.90
3. Suction Devices Plus Containment	1,000	2.50	735	1.10
4. Chemical Dispersant plus Containment	980	2.45	965	1.45
5. Sorbents/conveyor Plus Containment	1,580	3.95	1,130	1.67
6. Gellants/Conveyor Plus Containment	3,050	7.60	2,730	4.10
7. Endless Belt on Water Surface Plus Containment	2,000	5.00	1,000	1.50
8. Chemical Dispersant	470	1.20	760	1.10
9. Sorbents/Portable Suction Devices Plus Containment	1,200	3.00	900	1.35
10. Rotating Drums or Endless Belts (Non-Sorbent Surface) Plus Containment	2,100	5.20	1,050	1.60
11. Gravity Skimmer or Weir Plus Containment	1,760	4.40	940	1.40
12. Rotating Drum or Endless Belt (Sorbent Surface) Plus Containment	2,300	5.65	1,100	1.65

Condition	Index
Not affected by 1.6 ft. waves or debris	+0.5
Slightly affected by 1.6 ft waves or debris	0
Rendered inoperable by 1.6 ft. waves or floating debris	-0.5

Toxicity to Marine Life. Most chemical dispersants are toxic to marine life. Toxicity thresholds range from approximately 5 ppm to 10,000 ppm for presently used commercial materials.[4] The actual effect of using a specific dispersant in a given situation is dependent on the marine life present, the diffusion characteristics at the spill locale, the effectiveness of tidal flushing, the application ratio, and the physical characteristics of the spill material. Standards regulating the use of dispersants range from "unlimited" to "none permitted." FWPCA rules employed during the Santa Barbara incident permitted chemical dispersants to be used at ⩾ one mile off shore at concentrations equivalent to 5 ppm in the top three feet of water.

This FWPCA rule is reasonable in that it is based on typical diffusion rates, is safely below the toxicity level for most dispersants and assumes the dispersant is effectively mixed with the oil to provide some vertical distribution of the resulting oil-in-water emulsion.

The amounts of chemical required for emulsification is generally two to three times the manufacturer's recommendation–mostly due to the variance between field application and laboratory testing. A typical chemical dispersant must be used in the ratio 1:3 for effective use. This would correspond to effective treatments of oil slicks on the order of 5 x 10^{-4} in. (or less) in thickness. Bunker C, because of its high density, would never be expected to spread this thinly. Navy Special would attain such a thickness on the order of five hours after spillage. It is concluded that chemical dispersants, within the above framework, cannot be effectively used for spillage of Bunker C or Navy Special without exceeding most toxicity limits.

The indices to be applied to this criterion for system effectiveness evaluation were basically derived from the above reasoning. The applicability of chemical methods will depend on the circumstances of the specific spill situation and is exemplified for small spills as follows:

Spill Material	Spill Location	Surface Currents and Tidal Flushing	Index
JP-5	Berthing Areas	Adequate	+0.5
		Inadequate	0
	Open Water	Adequate	+0.5
		Inadequate	0
Distillate Fuel	Berthing Areas	Adequate	+0.5
		Inadequate	0
	Open Water	Adequate	+0.5
		Inadequate	0
Navy Special	All	All	0
Bunker C	All	All	0

Similar reasoning was applied to all of the various ranges of parameters during the "total effectiveness" compilation. For example, the indices for large spills (≤2000 gallons) were taken as (-0.5) for all cases clearly exceeding allowable toxicity ranges.

Availability. An effective system for removal of oil pollutants from the surfaces of harbor and port waters must, of necessity, be available for use when needed. Several factors influence the availability of specific systems:

1. Reliability–invulnerability to failure due to malfunction or damage by external forces (such as waves, currents, and collisions)
2. Maintainability–lack of dependence on special facilities or skills, ease of disassembly/assembly, and ready availability of replacement components
3. Portability–ability to quickly deploy to spill scene

Many of the systems to be studied have been extensively used and corresponding historical data are available. Other systems have not been used enough to provide a sound basis for juding these aspects. In the latter instances, the system will be analyzed on the basis of the experience with components involved, or similar components, to derive estimates of availability probability.

Systems estimated to be available 95 per cent of the time will given an index of +0.5 and all others will be given an index of zero.

Effectiveness Parameters

Effectiveness analysis involves assessment of each candidate system with respect to all effectiveness criteria over a range of conditions. These conditions may properly be called "parameters." They are the expected characteristics of spill incidents, the geographic and physical characteristics of spill sites, and the environmental conditions at spill sites. Representative ranges for these aspects were derived from available historical information and descriptive materials. The parameters selected for this study, and the rationale for their development, are given in the following paragraphs.

Size and Frequency of Spills. The frequency of spillage at a given site is important because very frequent spills can generate a chronic pollution situation if effective countermeasures are not routinely employed. For sites having very few spills, the cost of cleanup per gallon of spillage may be very high because of capital costs.

Navy installations servicing many diverse types of ships and involved in extensive fuel handling can be expected to have a significant incidence of spillage. The spillage can be due to casualty collision, personnel error (tank overfilling, premature hose uncoupling, etc.), and leaking tanks or piping.

The size range of spills from Navy vessels has been reported, based on a one year period, as less than 100 gallons to over 2000 gallons. Of the 117 spills during this period at two West Coast installations, more than half were less than 200 gallons and only seven were more than 1000 gallons. Information drawn from other sources on 147 spills over a 15 month period at San Diego indicate that 50 per cent of these spills were 20 to 100 gallons, 40 per cent were 100 to 500 gallons and 10 per cent were greater than 500 gallons. In 1966, some 67 spills from Naval vessels in the Long Beach-San Diego area were reported. Communication with the Puget Sound Naval Shipyard generally confirmed these values (about 20 spills/year at an average of about 200 gallons). It should be recognized that most of the above values are estimates –there is virtually no documented support which is known to have been verified by tank gauging.

For purposes of this study, incidents are classified into two representative size ranges: ≤200 gallons and ≥2000 gallons. These ranges are expected to encompass the vast majority of spill incidents and be representative of the extremes. Frequency of spillage was also classified in terms of extremes, ≥50 spills per year to ≤10 spills per year.

Petroleum Products. This study is concerned with the petroleum products in use by the Navy:

JP-5 Turbine Fuel
Navy Special Fuel Oil
Bunker C Fuel Oil
Distillate Fuel (new specification–expected to be used for most Navy craft sometime in the future)

Characteristic Harbor Water Movement. Surface and tidal currents can cause dramatic variation in the effects of an oil spill. Moderate tidal currents can carry a spill slick into vulnerable areas or away from them; enhance the effectiveness of dispersants; make a slick difficult or impossible to locate; and cause mechanical containments to be totally ineffective.

For purposes of this study, representative extremes will be considered as a parameter—largely as to the effects of currents on equipment effectiveness. These, with representative examples are:

		Examples
1.	Surface Currents and Tidal Flushing Minimal	Pearl Harbor Massachusetts Bay
2.	Surface Currents ≥0.5 knot and Adequate Tidal Flushing	San Diego Puget Sound Delaware Bay

Generic Identification of Potential Systems

The treatment and/or recovery of petroleum products released to a water surface can be by one (or a combination of several) of the following methods:

1. Chemical dispersion
2. Sinking with sorbent materials
3. Sorption or gelling
4. Physical retrieval
5. Burning *in situ*
6. Degradation (natural or enhanced)

Some of these methods, such as chemical dispersion, do not remove the oil from the marine environment, but rather only from the water surface. Dispersal or sinking can remove a potential fire hazard (when it exists) and minimize or eliminate many forms of damage to harbor facilities and waterfowl. However, the emulsified oil and chemical dispersants significantly increase the toxicity hazard to subsurface marine flora and fauna.

The equipment, materials, and techniques, described in the following sections, will be limited to those designed to cope with limited spills of petroleum products (i.e. up to a few thousand gallons).

Three discrete operational areas are identifiable with respect to oil spill treatment and recovery:

1. Containment
2. Chemical treatment and/or physical retrieval
3. Disposal of the recovered product

The three operational areas are essentially sequential and employ separate equipment, materials, and techniques. The systems to be considered do not necessarily entail operations within all three areas.

Potential Oil Treatment and/or Recovery System Combinations

The complexity of a recovery system varies greatly over the range of potential equipment, material and techniques. Three classifications of systems exist:

1. Chemical
2. Chemomechanical
3. Mechanical (or Physical)

Chemical methods include those which treat the slick with chemical agents or materials and do not require subsequent mechanical recovery. Included within this classification are methods employing chemical dispersants, burning *in situ*, enhanced degradation (biological or chemical), and sinking.

Chemomechanical methods include those which employ both chemical and mechanical or manual means of recovery. Included within this classification are processes in which the oil is sorbed or gelled and subsequently retrieved by mechanical or manual means.

Mechanical recovery methods are those which employ only mechanical or manual means to recover the product, such as skimmers, suction devices, and rotary drums or endless belts.

The delineation of total systems will include combinations of the general types of available equipment and materials within each classification. The potential systems identified within each classification will be examined both with and without oil containment devices. Systems to be considered will include both permanent and emergency containment installations.

Chemical Systems

1. Chemical dispersants applied directly to the slick with sufficient anxiliary agitation available.
2. System (1) + containment boom.
3. Chemical burning agents applied directly to the slick.
4. System (3) + containment boom.
5. Sinking agents applied directly to the slick.
6. System (5) + containment boom.
7. Enhanced degradation (exclusive of chemical dispersants) by the addition of microorganisms, etc.

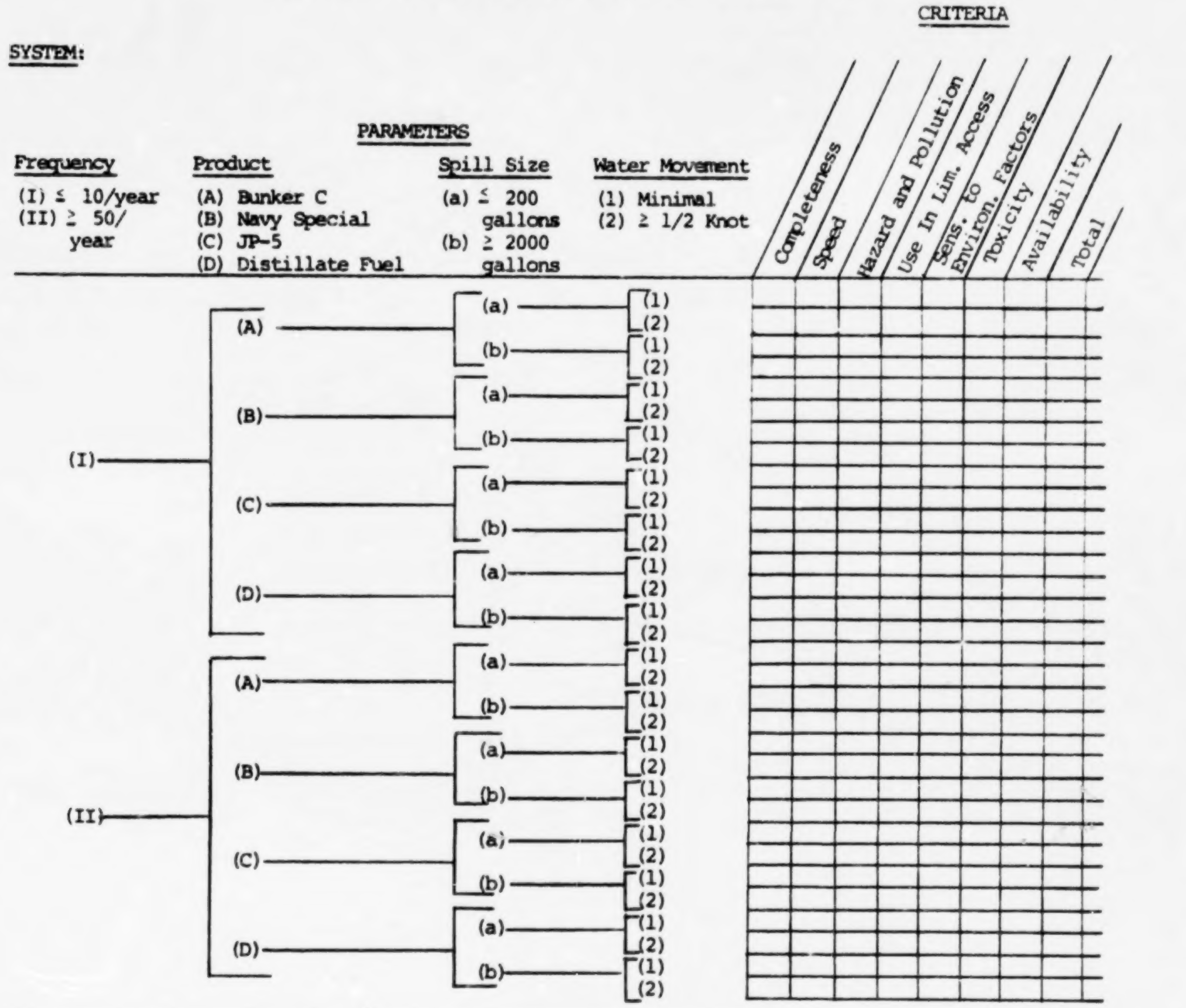
Chemomechanical Systems

1. Sorbents/suction pump.
2. System (1) + containment boom.
3. Sorbents/conveyor.
4. System (3) + containment boom.
5. Sorbents/manual retrieval.
6. System (5) + containment boom.
7. Gellants/conveyor.
8. System (7) + containment boom.
9. Gellants/manual retrieval.
10. System (9) + containment boom.

Mechanical Systems

1. Rotating drums.
2. System (1) + containment boom.
3. Endless belt.
4. System (3) + containment.
5. Suction devices.
6. System (5) + containment.
7. Advancing gravity skimmer or weir.
8. System (7) + containment boom.

FIGURE 1. EFFECTIVENESS ANALYSIS WORKSHEET


CRITERIA
SYSTEM:
PARAMETERS
Frequency
(I) ≤ 10/year
(II) ≥ 50/year
Product
(A) Bunker C
(B) Navy Special
(C) JP-5
(D) Distillate Fuel
Spill Size
(a) ≤ 200 gallons
(b) ≥ 2000 gallons
Water Movement
(1) Minimal
(2) ≥ 1/2 Knot
Completeness
Speed
Hazard and Pollution
Use In Lim. Access
Sens. to Environ. Factors
Toxicity
Availability
Total
(I)
(II)
(A)
(B)
(C)
(D)
(a)
(b)
(1)
(2)

Effectiveness Evaluation

The performance criteria and parameters which define the range of spill situations considered credible in this study have been combined to form a matrix, Figure 1, to enable a comparative effectiveness analyses of potential systems. Each worksheet refers to one postulated system; the sum of the index points for that system then is a comparative measure of the ability of that system to meet all of the criteria.

The comparisons of all systems indicates that 12 of the 27 systems considered are clearly superior (over 100 points) when all of the criteria are considered. The potential systems, in descending order of effectiveness, are as follows:

1. Sorbents/manual retrieval plus containment. (144)
2. Gellants/manual recovery plus containment. (144)
3. Suction devices plus containment. (144)
4. Chemical dispersants plus containment. (141-1/2)
5. Sorbents/conveyor plus containment. (128)
6. Gellants/conveyor plus containment. (128)
7. Endless belt on water surface plus containment (128)
8. Chemical dispersants applied directly to the slick. (126)
9. Sorbents/portable suction device plus containment. (120)
10. Rotating drum or endless belt (nonsorbent surface) plus containment. (112)
11. Gravity skimmer or weir plus containment. (112)
12. Rotating drum or endless belt (sorbent surface) plus containment. (112)
13. Sorbents/portable suction device. (82)
14. Gravity skimmer or weir. (81)
15. Chemical burning agents plus containment. (80)
16. Sinking agents. (76)
17. Sinking agents plus containment. (76)
18. Sorbents/conveyor (self-propelled). (75)
19. Gellants/conveyor (self-propelled). (74)
20. Suction devices (portable). (74)
21. Endless belt on water surface (self-propelled). (71)
22. Rotating drum (nonsorbent surface) (self-propelled). (51)
23. Gellants/manual retrieval. (50)
24. Sorbents/manual retrieval. (47)
25. Rotating drum with sorbent surface. (38)
26. Chemical burnings agents. (0)
27. Enhanced degradation (addition of bacteria, enzymes, etc.) (-24)

All but one (No. 8) of the above system employ containment for optimum effectiveness, and even this system is improved when a boom is employed. It is, therefore, apparent that containment of the slick is desirable in virtually every spill of petroleum products. The principal variation among mechanical systems is their capability to function in limited access areas.

It must be recognized that the effectiveness summation covers system performance over a wide range of spill situations and, therefore, the superior systems are applicable to Naval installations in general. Certain Naval facilities, where the range of parameters is greatly restricted, may be evaluated in terms of the parameters or restrictions unique to that facility. For example, facilities (such as Naval Air Stations) in which spills of only one or two of the products considered are likely, should be considered on an individual basis to select optimal systems.

Other controlling factors which can exist in individual facilities include: state or local pollution control regulations, port or harbor authority policy, the proximity of valuable shellfish or fin fish areas, or recreation beaches. Any of these factors can eliminate an otherwise effective system from contention.

It should also be recognized that in some cases the criteria can vary with the parameters. For example, much more relative speed is required for a large spill with a considerable amount of water movement than for a small spill under similar conditions.

The parameters can also have different implications depending on the type of system being considered. For a chemical system, moving water aids in dispersing to a point that the spilled material will not reappear and cause further pollution, while in a mechanical system the water movement is a hinderance.

An example of the interdependence of criteria is that in situations where currents are significant, the speed and completeness of treatment are inter-related in that completeness is not possible unless the slick can be recovered very rapidly, especially with a light product. Hazard and pollution are related to speed and completeness when the water is moving because objects distant from the source can be contaminated if the recovery is not effected immediately and completely.

Other notes of this type, developed during the effectiveness compilation are given in the following paragraphs:

Completeness of Removal

Chemical System. Implies that the oil is essentially completely dispersed from the water surface and does *not* reappear at a later time. This means that in calm or unflushed areas the chemicals do not necessarily do a complete long term job as they may reappear.

Chemomechanical and Mechanical Systems. Implies that the system removes the oil from the water surface before it spread or drifts out of range. Therefore, these systems must operate more rapidly on spills of lighter products. Also, the system must be capable of removing the oil accumulated around obstructions or booms. This is not the same as operating in limited access areas. For example, rotating drums have little or no ability to draw heavy or very light oils from the surrounding area and therefore, will not do an essentially complete job.

Speed of Removal

Speed often is an essential factor in completeness, i.e., the slick will spread too thin if it can't be recovered in time. Speed also implies that the work can be done within daylight hours.

Hazard and Pollution. Includes water surface pollution to waterfowl, facilities and private boats (i.e., damage to recreation such as swimming), fire danger, and air pollution.

If a chemical dispersant reappears some time after treatment the pollution can be great.

Sinking agents which release the oil at a later time are similarly ineffective.

System Use in Limited Access. Ability to maneuver and get into tight spaces. Also ability to pick up accumulated oil off a boom and operability in shallow water for mechanical system.

Sensitivity to Environmental Factors. Is the *system itself* sensitive to waves, etc., or does its *capability* for retrieval decrease?

Toxicity. Applies only to chemicals. Toxic when spread over a small area with minimal tidal action or currents. Excludes waterfowl.

Availability. Any self-propelled system must be penalized in this respect because the propulsion unit is bound to break down or require periodic maintenance. Portable gear is superior because it can use other vessels. Also outboard motors are preferred because they can be replaced.

Cost Effective Analyses

Assumptions and Basic Costs

The systems that best fulfill the performance criteria for the full range of parameters are to be economically evaluated. The cost base chosen was dollars per gallon of oil treated or recovered for each of two spill situations: (a) infrequent (≤10 per year) small spills (≤200 gallons) including one spill up to 2000 gallons, and (b) frequent (≥50 per year) small spills (≤200 gallons) and infrequent (≤10 per year) large spills (up to 2000 gallons).

Only systems capable of rapid application after a spill incident were evaluated, because it is impractical in most Naval installations to provide permanent containment barriers in all areas that a spill could occur. Thus, pneumatic barriers, which provide an efficient (although not necessarily inexpensive) means of containment, were not considered because of the lack of emergency deployment capability.

The cost in dollar/gallon of oil treated varies with the spill size and frequency as shown on Table 5. The parametric cases used in these analyses are believed to represent the most probable situations–they are intended

TABLE 6. COST EFFECTIVENESS RATIOS

SYSTEM	Effectiveness Index Score	Cost/Gallon		Cost Effectiveness Ratios	
		A (one 2000 gal + 10-200 gal Spills/yr)	B (10 2000 gal + 50-200 gal Spills/yr)	A (one 2000 gal + 10-200 gal Spills/yr)	B (10 2000 gal + 50-200 gal Spills/yr)
1) Sorbents/manual retrieval plus containment boom.	144	\$2.65	\$1.60	0.0184	0.011
2) Gellants/manual recovery plus containment boom.	144	5.00	3.90	0.0347	0.0271
3) Suction devices plus containment boom.	144	2.50	1.10	0.0174	0.0076
4) Chemical dispersants plus containment boom.	141-1/2	2.45	1.45	0.0173	0.0125
5) Sorbents/conveyor plus containment boom.	128	3.95	1.67	0.0308	0.0131
6) Gellants/conveyor plus containment boom.	128	7.60	4.10	0.0595	0.032
7) Endless belt on water surface plus containment boom.	128	5.00	1.50	0.0391	0.0117
8) Chemical dispersants applied directly to the slick.	126	1.20	1.10	0.00955	0.00875
9) Sorbents/portable suction device plus containment boom.	120	\$3.00	\$1.35	0.025	0.0125
10) Rotating drum or endless belt (non-sorbent surface) plus containment boom.	112	5.20	1.60	0.0464	0.0143
11) Gravity skimmer or weir plus containment boom.	112	4.40	1.40	0.0393	0.0125
12) Rotating drum or endless belt (sorbent surface) plus containment boom.	112	5.65	1.65	0.0415	0.0147

to represent Naval installations at ports which have a large volume of traffic and fuel transfer operations on the one extreme and those with nominal activities on the other. Cost data were combined with the effectiveness indices by simply dividing the cost/gallon of oil treated by the total effectiveness index for each system. These are shown for each of the twelve most effective systems on Table 6. On this table, the system having the lowest cost/effectiveness ratio is the most favorable.

It can be seen that for the more frequent spill case, systems 8, 4, 3, and 1 are the most cost effective. For lower frequency of spillage, systems 3, 8, 1, and 7 are superior. Summation of the cost effectiveness ratios for the two spill frequency situations shows systems 8 and 3 to be most cost effective.

It is concluded, that within the present state-of-the-art, direct application of chemical dispersants (system 8) and a system utilizing a suction device plus a containment boom (system 3) are, overall, most cost effective. Each of these two systems would be expected to be more effective in some situations than in others.

The most advantageous system for all parameter combinations, except for moderately severe sea states and/or significant tidal flushing and surface currents is the one consisting of a mechanical suction device plus containment booms. For storm conditions, it is reasonable to assume that no oil treatment activities would be attempted. Where local, state, or federal regulations prohibit the use of dispersants, this system should also be employed. If tidal flushing is significant and no contrary restrictions exist, chemical dispersants applied directly to the oil slick, with auxiliary agitation should be used. At most Naval installations where frequent spills have been experienced, both methods should be available—with the mechanical system used when the spill can be contained under calm sea conditions. The dispersant system should be used during periods of tidal flow or moderate sea conditions. If both systems were available, the use of booms, which are part of the mechanical system, would be beneficial for use with the dispersant system.

It should be noted that Bunker C at low temperature is probably not amenable to treatment by any of the systems considered in this study. If it is below its pour point (30 to 60°F) Bunker C cannot be effectively pumped, mechanically picked up, or mixed with dispersants or sorbents. Under this condition, spills of this material can probably be treated only by manual retrieval. This does not appear to be totally undesirable when the physical characteristics (congealed, nonspreading, nondiffusing, slow moving) and the associated minimal threats to marine life and property are considered.

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Oil Soaked Straw Harvesting Techniques

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Abstract

The use of straw as an adsorbent material in the mechanical recovery of oily pollutants is reviewed with emphasis given to existing methods for the harvesting of the oil soaked straw. State-of-the-art harvesting techniques, while admittedly crude and needing improvement, is complicated by the wide variety of conditions and subtleties encountered in oil pollution incidents. The development of oil soaked straw harvesting equipment, possibly by the agricultural implement industry, to be used by various types and configurations of vessels will permit greater usage of the demonstratably effective application of straw in oil pollution incidents.

Several methods exist for combating accidental oil spills. The mechanical recovery of oil by physically picking it up either with skimming or vacuum pumping devices or by introducing sorbent material into the oil slick for subsequent recovery is preferred by many over other methods of either dispersal of the oil through the use of chemicals or sinking it through the use of various agents. Ignition and burning of volatile oils may be feasible if existing conditions show this action is warranted.

Mechanical recovery is accomplished by using one of several types of sorbent materials. The selection of an adsorbent and its use in an oil pollution incident is contingent upon a number of factors, not the least of which is the economics concerned with the utilization of the material including its availability to the site and the energy requirements necessary to introduce the material into the oil slick and its subsequent removal and disposal. A prime prerequisite of a good adsorbent is its capacity to collect upon its surface a maximum amount of the oily pollutant and yet still remain afloat. Collection and removal from the water of the oil soaked material can be accomplished only if it remains accessible.

Of the many collection agents used in absorbing oily pollutants from water, one stands out among all others by reason of its capacity to gather up to five times its own weight of an oily pollutant and still remain afloat. It is also almost universally available at very low relative cost. This material is straw, preferably long cut wheat straw of the Durham, Marquis, Red Fife or Kitchener strains. Baled straw is also entirely satisfactory as the long cut wheat straw is rapidly becoming a thing of the past in most countries where mechanization of the harvesting operation is an accomplished fact.

The cellular construction of wheat straw, which can be compared to bamboo but in a miniature form, incapsulates air pockets that provide considerable buoyancy to this collection agent. The biologists call this cell structure monocotyledon or monocots. The monocots include such diverse families as the lillies, palms, grasses, and orchids and number about 50,000 species. Of these, straw has been found to be the most satisfacotry for adsorbing oil.

The dispersal of wheat straw into oil slicks is readily accomplished using mulching equipment that has long been the standard in the erosion control industry. Needless to say, there are certain techniques that have to be followed in the dispersal of straw from mulching equipment. One of the principal concerns is the necessity to utilize the winds prevalent at the scene of an oil spill incident by mulching downwind, rather than is sometimes tried, mulching directly into a stiff wind. Dispersal of three to five tons of straw per hour from one mulcher is quite feasible and depending upon method of locomotion, that is, either by boat or behind a truck operating on the shore, approximately 2-½ acres or 100,000 square feet can be covered per hour.

After the mulching operation into an oil slick has been accomplished, it has been found that a ripening interval of from three to six hours is required for the maximum adsorption to occur prior to harvesting of the oil soaked straw. Initially, the sea or body of water that has been subjected to a thorough mulching operation using long cut wheat straw is golden in color and seems deceptively firm where wave action is minimal. Within an hour small islands of straw, or calving, will appear indicating the straw is ripening or collecting the oily pollutant. Where wave action is moderate or where there is agitation of the mulched straw, the ripening interval is shortened by reason of the churning action of the collection agent and the oily pollutant.

After a sufficient ripening interval in which it has been determined by inspection that the straw has adsorbed the maximum amount of oily pollutant, it is desirable to remove the straw physically from the water in the most expeditious manner possible. Now, "here's the rub". While straw can be mulched over large areas of water quite rapidly from ship and boat mounted equipment or even from the shore or from piers, the state-of-the-art of collection and subsequent removal of the oil soaked straw is just now maturing. The importance and value of immediately confining an oil slick by the various types of booms or barriers either commercially available or that can be hastily assembled is so apparent that it goes without saying that one of the first acts in controlling an oil slick is its containment.

Oil booms or barriers employing weighted skirts and a buoyant fin to provide freeboard have been used to collect and concentrate the oil soaked straw but, by and large, have not proven too successful in anything other than calm seas because of the ever-present broaching of the oil boom by the oil soaked straw or even, in some cases, of the pollutant passing under the oil boom when it is being towed at any more than a dead slow speed. Long narrow nets towed between two vessels have proven successful in the collection of oil soaked straw when used in conjunction with oil booms or barriers. After the oil soaked straw has been concentrated the task of removing it from the water is obviously less difficult.

The standard method used in removing oil soaked straw from water is presently manpower with suitable rakes and appropriate containers. It is necessary to get personnel, often in large numbers, right down into the concentrations of oil soaked straw in small boats or on floating platforms to rake and otherwise lift the straw into suitable containers, say 55 gallon drums, that can be then lifted and dumped into larger collection hoppers aboard vessels or into dump trucks if it is possible to work in proximity with the shore. Conveyor systems using wide neoprene or stainless steel belts are being developed specifically for use in the recovery of the oil soaked straw from rivers, lakes, and coastal waters. Mounted off the bow of workboats with not more than three feet of freeboard and hydraulically operated in both the speed of the belt travel and the positioning into the oil slick, these conveyor systems have shown promise in recovering oil soaked straw for disposal into hoppers carried on the workboat in quantities considerably in excess of what can be recovered by a crew of eight to ten men by hand..

Even with conveyor systems, however, it is necessary to have personnel assist in feeding the straw to the conveyor system and to remove large flotsam and debris such as logs, poles, tires, etc. from fouling the conveyor system. When the oil soaked straw is considered in the light of it being just another problem for material handling systems and equipment is designed and put into use for the specific parameters about which the equipment has been designed and built, there is a fairly good chance that conveyor systems will perform as intended. However, there are a host of everchanging factors attendant with most oil spills; and any one of these factors can affect drastically the efficiency of the oil recovery operation be it weather including wind and sea conditions, the physical condition of the oil-water emulsion, or the proximity of structures such as piers, wharves, jetties, or other shoresite construction.

Polurethane foam has been investigated as a sorbent material and, initially, enthusiasm was generated for the potential offered by both the rigid, which has been used in slabs, in shreaded form in mattresses, and in the flexible soft type which has been employed at different pore densities in roller drum application. Its possible re-usability was an attractive asset. Unfortunately, the theoretical potential of this material has not yet been fully borne out by the reduction to practice. This is so often the case in any oil recovery operation.

I am often asked during oil spill confinement and recovery operations by both the news media and the many spectators at the scene of an oil pollution incident if there isn't anything better than straw. The logic is, I assume, that now with the great technological advances made by industry on every other front, there surely should be something "better than straw."

Now let's examine what is meant by the statement, "better than straw." There are materials, some of them reusable, most of them manmade, that have an adsorbency similar to straw but with a corresponding greater cost per ton delivered to the site. Some of these, such as the shreaded rigid polyurethane foam, present the same, if not more, difficult problems of retrieval as straw and are at present not generally available on an emergency basis when the occasion does arise for their use. Regardless of the type of adsorbent used, the principal problem is one of harvesting. The advantage of having harvesting equipment for oil soaked straw or other adsorbent material that may be rapidly transported to the scene of an oil spill incident and used over the side of a variety of types of vessels becomes most decidedly apparent in a major oil spill incident.

In my experience, there is usually no shortage of water craft at an oil spill, only a lack of the proper tools which include the containment and harvesting equipment. The agricultural implement manufacturing industry has long been faced with and has successfully resolved, the many diverse problems of harvesting a variety of crops. My investigations with several implement manufacturing concerns indicate it would not be too difficult to develop suitable ship-borne harvesting units for the collection of oil soaked straw and other adsorbent material. The only present obstacle to the development and reduction to practice of the more sophisticated oil soaked straw harvesting devices is funding.

I am confident that this matter will be resolved in the very near future when the importance of having this mechanical equipment on hand for major oil spills is realized.

The recovered oil and oil-water emulsion soaked straw does not necessarily have to be brought aboard the vessel employing the harvesting equipment since it may prove hazardous and involve the craft in a conflict with its documentation by regulatory agencies. For example, the Rules and Regulations for Tank Vessels Subchapter D of the U.S. Coast Guard could be well handled by being pumped into the large inflatible rubber bags marketed by several rubber companies and towed or left for other vessels to convey to shore.

So again, the question comes back, isn't there anything better than straw? To which my reply is usually that in the context of all economic factors considered, one rival that straw may have as an oil adsorbent when the fact of dollars per ton of recovered oil is considered is another agronomical product that is just now undergoing experimental use and is "promising." That is shreaded corn cobs. Corn cobs, or maize as the British prefer to call it, are an agricultural by-product which in the Midwest are usually burned when the corn has been shelled for lack of any appreciable value. The adsorbency on the four to one ratio just about equals that of straw. However, the major drawback is lack of availability except in corn producing areas and delivery in an unpackaged state. Straw at least has the advantage of being delivered one way, in a packaged condition if it is only by means of baling twine. I believe that corn cobs both shreaded and whole deserve more experimentation to determine their actual potential as an oil adsorbent for possible future use in oil spill incidents. If I appear to favor straw in the mechanical recovery of oily pollutants, it is because, in my opinion, straw has proven its utility better than any alternative offered today.

Until something comes along that is better than straw, that is as cheap as, is practically universally available, presents no more difficult problems of dispersal or collection and has the capacity to adsorb up to five times its own weight without sinking, then we shall use straw and be grateful that we have it.

Good Salvage Operations-

Key To Preventing Oil Pollution

Paul Preus
President, Clean Water, Inc.

When a tank ship, cargo ship, oil barge or shore pipeline has a casualty, time is of the essence in making the remedial repairs, thus lessening the severity of the initial casualty.

I would like to make the following classifications of casualties:

TYPE A casualty is one where the ship's crew can handle the situation and a small pollution problem exists, however, the ship's crew, by means of utilizing ship's pumps, portable pumps and pollution control techniques, can keep the vessel or equipment "oil-tight." This Type A casualty would require the immediate notification of the Federal Water Pollution Control Administration, the United States Coast Guard, the United States Corps of Engineers and the state and local pollution authorities, and the U. S. Customs. Thus, the appropriate agencies would be informed and could monitor the casualty.

TYPE B casualty and pollution problem would be where a vessel has to have a salvage master and/or pollution control expert on scene to put into effect *full* pollution control procedures, which includes making temporary repairs to the hull or pipe lines to prevent the oil from leaking out and once oil has leaked out, to deploy a suitable oil boom to contain the pollutant and harvest the crude oil or heavy fuel off the surface of the water. The governmental agencies as mentioned in a Type A casualty would be notified and they in turn would have their on-scene representatives to assist the salvage master and pollution control expert in the corrective measures that would have to be taken to rectify the pollution problem because the ship's crew cannot handle the situation with equipment and personnel on board.

When a Type B or C casualty situation is in effect, the salvage master and/or pollution control expert should have a duly-signed agreement of either Lloyds or U. S. Open Form, which means that a contract of salvage is signed by the master of the ship and he is at this time an agent of necessity and signs in behalf of the ship and its cargo. The amount to be paid the salvor is left open and settled by arbitration. Thus, the salvage master can effectively direct the salvage and pollution operation without the great problems that arise when the ship's captain, owners and operators have to give their approval on every item of expenditure before the necessary items are obtained and are on the scene and in use. However, if a per diem is agreed upon, the salvage master and/or pollution control expert should have the owner's authority to proceed un-hindered to accomplish pollution control and salvaging of the vessel.

It would be helpful if the underwriters of Hull and the P.&I. mutual associations agree on a "general average" on a B or C type casualty, as the work that is accomplished in behalf of P.&I., helps Hull and vice-versa. P.&I. (Public and Indemnity), is a mutual association that protects the owner of the ship and cargo owners from liability claims against them.

TYPE C casualty pollution problem and salvage problem requires a salvage master and/or pollution control expert on the scene with the immediate notification of the U. S. Coast Guard, FWPCA, Army Engineers, U. S. Customs, the state and local pollution authorities. This Type C casualty would require complete salvage vessel assistance with supporting equipment, including barges or smaller tankers for off-loading when weather and sea conditions permit. Bear in mind, a Type C casualty could present a problem of pollution when the vessel or barge is in a hazardous position and it may be necessary to put an air bubble in enough compartments to re-float the vessel, thus saving the vessel or barge and preventing the vessel or barge from breaking up and causing a greater pollution problem. It would be

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understood under this salvage operation that any oil that had to be discharged would be removed from the surface of the water.

We must bear in mind that under a C type casualty, if the vessel is carrying hazardous materials, the Federal Water Pollution Control Administration must have their representative on the scene twenty-four hours a day, as it may be in the best interests of the ship's safety and the country's best interest to neutralize the hazardous material or pump it over the side, or pump it into appropriately equipped chemical-carrying vessels or barges. Bear in mind that hazardous materials either float on water or sink, or are soluable in water. I would recommend that in a Type C casualty where hazardous materials are involved, that a Certified Marine Chemist be retained as a consultant to the Salvage Master.

In 1962 there was a C type casualty, namely, the *M/V Tarentel,* beached off Cape Henry, Virginia. We had to utilize a non-flammable, non-solvent emulsifier dispersant to chemically clean and emulsify and disperse diesel oil, No. 5 oil, and lube oil that was floating on the water in the flooded engine room. Thus, we were able to burn through a 3 in. thick deck to make an excess opening so that a diver could reach the forward bulkhead of No. 4 cargo hatch and jam wedges around the diesel air tank, thus enabling the portable pumps to keep the water out of No. 4 cargo hatch. This was accomplished and in about nine hours the ship was afloat and towed into Newport News, just ahead of a 20 to 30 knot Northeaster. There was no oil pollution during the salvaging and repairing of the *M/V Tarentel.*

Another C type casualty was the *M/T Honnor,* which had her starboard side opened from No. 3 starboard wing-tank through No. 6 starboard wing-tank, including her after pump room and adjacent cofferdams. We met her under tow off Sandy Hook and we immediately washed down her decks and bulkheads with a degreaser to provide safe working conditions on deck. She was anchored in Raritan Bay and upon anchoring, two sea tugs were tied up on her starboard side for pollution control work. Barges were immediately brought alongside and as soon as the hoses were connected, the Chief Mate and I started the forward pump in the forward pump room and as a result, we had a very fast discharge of her remaining cargo. By utilizing pollution control techniques of portable pumps and skimming devices, the ship was towed to a tank cleaning plant at Hoboken, New Jersey, and the ship was gas-freed and then she proceeded to an American shipyard for full repairs. During the initial barge discharge, the U. S. Customs were very helpful in expediting the necessary paper work.

The *M/T Sigdahl* was also a C type casualty as she was aground, loaded with heavy fuel, off 38th Street and the East River. This presented quite a problem as there was a tug and barge strike at that time and through the combined efforts of the towing companies, barge operators and the unions, both tug boats and barges were along-side in a matter of hours. We immediately started to off-load part of her cargo by utilizing the barge's pumps to off-load the tanks that were ruptured on the bottom. Because of this very prompt off-loading, the heavy fuel did not cool down and we were able to put into effect complete pollution control procedures. The ship then proceeded, with only a day and a half delay, to her original discharge terminal and upon the completion of her discharge, she went to sea and gas-freed all tanks and compartments and then proceeded to a shipyard in Baltimore, Maryland where she was immediately dry-docked and surveyed and fully repaired. After the initial grounding of the ***Sigdahl,*** there was no oil pollution during the barge off-loading or while she discharged the remainder of her cargo at her assigned pier terminal or when she was dry-docked in Baltimore.

The *M/T Stolt Dagali* was a C type casualty as she was cut clean across. The aft engine room, 9 center and after port wing-tank immediately sank. The forebody took a list and a drag aft, and on Thanksgiving Day, a sea tug took her in tow and she was anchored in the lower bay of New York Harbor. As soon as she was anchored, I had the U. S. Customs seal all valves and tank expansion trunks. Then all the interested parties were on board at the same time to take their cargo samples. On the foredeck her cargo was heptane, polypropylene tetramar, and metharol, and aft, she had one tank of peanut oil, one tank of safflower oil, and the rest of the cargo was coconut oil. We had to gas free the forward pump room and lining up to discharge was no easy job, I assure you. All her cargo was safely discharged and we gas-freed the fore-deck tanks using cold water and a non-solvent emulsifier and dispersant that contained no chlorides and no phosphates.

The *M/V Emstein,* a cargo ship, was a C type casualty, as she went afire after she was hit by another ship in the St. Clair River near Sarnia, Canada. She had cargo on board that was very active when it was in water, other cargo went afire after it became wet and started to dry, while other cargo would react when other liquid cargo came in contact with it. In addition, she had many 30 gallon drums of cobalt stored in the cargo hatch forward of the midship house. By using good salvage diving techniques (which includes experienced hard-hat divers with appropriate staging and hog lines secured, thus enabling an efficient survey of the hull damage), tapered plugs, wooden wedges and mattresses, the hole that flooded her engine room was plugged well enough so that the engine room and aft shaft alley were pumped out. During the pumping operation, I chemically cleaned the engine room to gas-free it. The prime purpose was to eliminate any fire hazard and to clean and preserve her main engine, auxilliaries and all electric motors. Thus, her engine room was safe for repair work when she reached the shipyard.

The *M/T Tore Knudsen* was very much a C type casualty as the tide in the St. Lawrence River in early April caused her to bottom on some rocks and when the high tide came, the good Lord was with her and she came off floating. However, it took all the pumps in her engine room to keep her afloat and she was tied up at Wolf's Cove, Quebec City. Additional portable pumps were rushed to her and we immediately lined her up for fast discharging of her cargo. There was no oil spill during this off-loading operation and gas-freeing operation due to strict pollution control practices.

The *M/T Algol,* February, 1969, was also a C type casualty as she bottomed and holed seven wing-tanks and flooded both pump rooms and their adjacent cofferdams.

The weather in Buzzard's Bay was cold and rough, however, and over 45,000 barrels of her heavy fuel cargo were safely discharged without any large oil spills and strict pollution control procedures were in effect.

An oil boom made of 30 ft. long telephone poles laid side by side with 1 in. waterproof plywood secured between them so that approximately 2 ft. of the plywood was in the water, with waterproof canvas making an oil tight connection between each section of the telephone poles. This telephone pole oil boom was secured from the starboard side in way of No. 8 starboard wing-tank and then around the stern to the outboard side of the barge that was tied up on the port side of the *M/T Algol.* There was very little oil in the confines of the oil boom, but what did get in when a hose broke, was quickly absorbed using a sorbent material, even with the water temperature at 34°F. The absorbed oil was harvested out of the water without trouble. In addition, this sorbent material was used on deck in the vicinity of the portable pumps and hose connections and as a result the oil that leaked on deck was rapidly absorbed and did not present a slip hazard, and the absorbed oil was shoveled off the deck into empty barrels. The ship was then at anchorage in Buzzard's Bay and we had a Northeaster with winds 30 to 40 knots plus seas of 20 ft. along with a snow-fall of 3 ft. During this storm several 1 in. wires parted and the telephone pole oil boom was towed in sections back to New Bedford as soon as the weather subsided. However, the oil boom had served its purpose for about six days and there was no oil pollution in Buzzard's Bay.

The *M/T Algol* was given permission to be towed to New York Harbor after all her holed tanks had the cargo oil pumped off and skimmed off. After arriving at the dock in Bayonne, N. J., the remaining cargo of approximately 78,000 barrels of heavy fuel oil was safely discharged as we operated her main cargo pumps with steam under water. While the *M/T Algol* was at Buzzard's Bay, we had a contingency plan to handle a large oil spill by utilizing commercial fishing boats to harvest the absorbed oil off the surface of the water with half-inch diamond shaped nylon fishing nets. The absorbed oil was given to the road department to use as a bottom burm over stones for road building.

The *S/T Chelwood Beacon* that was aground about five miles at sea off Sandy Hook was a most interesting salvage operation, and I spent four of my roughest days at sea on this grounded and dead ship, in a cold January. She dug herself in an approximate twelve foot hole as a result of this storm and when the weather subsided, oil barges were brought alongside and in the beginning the barges' pumps were used and then portable pumps were used on air pressure to safely discharge her cargo. After twenty days of off-loading when weather permitted, she was towed to port. If an air bubble procedures was initially used, it would have meant that at least 30,000 barrels of oil would have been discharged into the ocean and this oil would have covered a very large part of Sandy Hook and the New Jersey shore beaches. I am happy to say that oil pollution control procedures as mentioned previously were strictly adhered to, and as a result there was minimal pollution during the entire off-loading of the fuel cargo on the *S/T Chelwood Beacon.*

In closing, I would like to make these recommendations: 1. that a special effort be made to have the FWPCA establish a hazardous materials center that would have all the known hazardous materials and their ingredients listed and catalogued so that in an emergency, they could have competent persons recommend the safe neutralizing or inerting of the hazardous materials in an emergency situation; 2. that when a casualty occurs at sea or in a bay or harbor waters, the U.S.C.G. because of their knowledge, seamanship, search and rescue capabilities, provide fast transportation and closed communications, should be called to see to it that competent persons can be on the scene of the casualty as soon as possible; 3. that the Army Corps of Engineers provide their equipment and manpower when requested, especially on weekends and holidays and when manpower is needed in a hurry to accomplish the pollution control operations. They, of course, will be compensated for their service; 4. that the U.S.C.G. provide closed communications thus avoiding wrong information about the casualty reaching the public.

Confinement And Control Of Oil Pollution On Water With Monomolecular Surface Films

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Abstract

Under favorable conditions monomolecular surface films can be used to guide, confine and condense petroleum spills on water. Composed of water-insoluable, non-toxic organic material, these films spread rapidly and spontaneously into a one-molecule-thick layer. Consequently, small quantities of piston-film material will clear thin oil layers from large areas of a water surface. The effects of wind, the chemical character of the pollution and its thickness upon the usefulness of the piston film will be discussed. In addition to clearing water surfaces of oil, one of the most useful applications may be the ability of the surface film to confine and condense a small oil spill into layers as thick as one centimeter. Since the petroleum is thickened and compressed into a much reduced surface area, the efficiency of oil retrieval techniques would be enhanced.

In the major international problem of petroleum pollution of water bodies, current emphasis is being directed toward three primary goals–prevention, containment and recovery. Dispersion of sinking techniques may well be relegated to minor roles in future assaults on oil spills since they do not remove but further distribute the pollutant into the aqueous environment. Unless it can be shown that biological degradation of the oil is significantly enhanced by dispersal and that the dispersing agent as well as the petroleum contaminant is universally non-toxic to aquatic life, the danger exists that poisoning and saturation of the water environment may eventually result. However, chemical techniques should not be considered undesirable as long as the chemical additive is itself a nonpollutant and the petroleum spill is contained in a suitable condition for subsequent retrieval. One such approach is the generation of water-insoluble, monomolecular films to confine, condense and control surface oil pollution.

Some control of oily surface pollution can be achieved with a piston-like artificial slick which spreads spontaneously into a one-molecule-thick layer. The piston film compresses the oil into a thicker lens occupying a smaller surface area thereby facilitating retrieval and surface cleaning operations. The use of such surface spreading agents was first studied by Zisman[1] as a possible technique to drive oil from the vicinity of sinking ships. The author deemed the method to be of limited value because of the great oil-thickness in the vicinity of the ship subsequent to the spill. Sigwalt[2] also proposed the use of a fatty acid film to neutralize the spreading of oil although no study was made of the limitations of the technique or of the chemical variables involved in selecting the most effective piston film. The validity of the piston film approach and the conditions under which it is applicable to current oil pollution problems will be determined by considering:

1. The surface chemistry of petroleum products on water bodies,
2. The effects of oceanographic and meteorological parameters on the spreading properties and oil-confinement characteristics of the monomolecular control films, and
3. Field demonstrations of the method applied to freshly spilled and weathered oil pollution.

Surface Chemistry of Petroleum Products on Water

In general, pure hydrocarbons do not spread spontaneously onto a water surface. Only the low-molecular-weight hydrocarbons spread readily and exert a positive spreading pressure[3] rather than remaining on water as a liquid lens. The spreading pressure of an oil on water, F_o is defined as:

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[1] Superior numbers refer to literature references at conclusion of text.

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$$F_o = \gamma_w - (\gamma_o + \gamma_{ow}) \qquad (1)$$

where γ_w = surface tension of water,

γ_o = surface tension of oil,

γ_{ow} = interfacial tension between the oil and water.

Aliphatic hydrocarbons more volatile than n-nonane and most aromatics have small positive F_o's (spread) while none of the cyclic hydrocarbons spread spontaneously, i.e., their spreading pressures are negative. When petroleum spills occur, the volatile rapidly spreading components evaporate leaving behind a complex mixture of the higher-molecular-weight hydrocarbons, as well as surface-active compounds containing primarily oxygen and sulfur. When the surface active constituents of the oil adsorb at the oil/water interface, the hydrophilic polar portion of the molecule is associated with the water surface while the nonpolar or hydrocarbon portion of the molecule is oriented into the petroleum oil. It is these surface-active components which cause the otherwise nonspreading hydrocarbon oils to thin out into oil slicks whose thickness may be qualitatively estimated from their appearance (Figure 1). The extent of spreading is a function of the quantity and nature of the surface-active components of the oil.

If the water surface is already occupied by a surface film (natural sea slick or existing surface-active contamination), spreading of the oil may be retarded. Further, surface currents driven by wind, waves and convectional cells determine the shape and direction of movement of the oil spill.[4] The spreading tendency of the oil against external forces (spreading pressure) is dependent upon the quantity of surface-active material in the oil. For example, 0.2, 0.5 and 1.0 per cent dodecanol-1 dissolved in paraffin oil ($F_o < 0$) gave spreading pressure values for the respective mixtures of 3.0, 11.0 and 17.5 dynes/cm.[5]

The sources and properties of five possible oily pollutants are listed in Table 1. Spreading pressures of the oils were determined by the piston monolayer technique of Zisman.[5] The rather high values of 25-33 dynes per cm. on seawater (Table 1) were due to the polar, surface-active components in the oils. Spreading pressure values between 17 and 27 dynes/cm have also been reported for various crude oils on fresh water.[6] These petroleum products will spread readily into thin films on a clean water surface unless external chemical agents or physical processes are present to exert a counter force against the spreading tendency of the oils.

Properties of Monolayers for Oil Pollution Control

The effectiveness of water-insoluable monomolecular films to control or contain oil spills depends upon location and the geophysical conditions under which they are to be applied. Several liquid monolayer-forming materials were rated for their ability to spread rapidly and spontaneously into a monomolecular film, to spread against wind and to contain oily pollution as a thick unspread lens. Under the conditions of application in the field, the surface film is supplied from unspread liquid lenses of material which are in equilibrium with the monolayer. Since the excess drops of liquid film-forming chemicals do not spread on their own monolayers, they act as reservoirs to replace losses from the control film and to expand its size.

The spreading velocity of most water insoluable monolayers has been shown to be a direct function of spreading

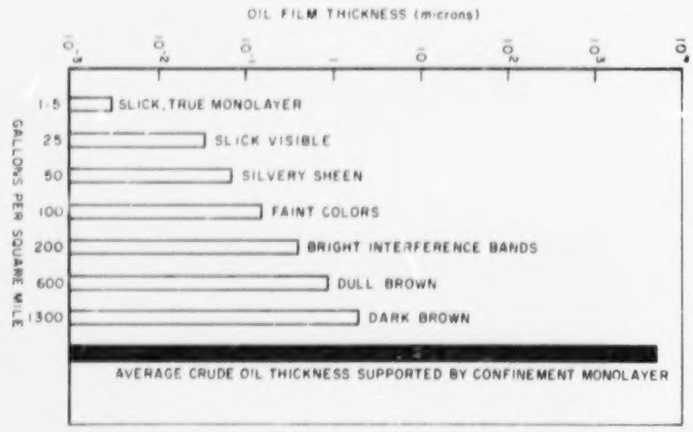
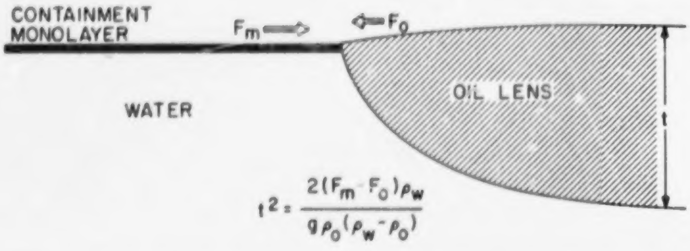


Figure 1. Qualitative relationships between oil film thickness and appearance of oily water surface. Thickness of average crude oil confined by a surface monolayer with a film pressure of 40 dynes/cm.



$$t^2 = \frac{2(F_m - F_o)\rho_w}{g\rho_o(\rho_w - \rho_o)}$$

Figure 2. Schematic of oil lens in equilibrium with monomolecular surface film.

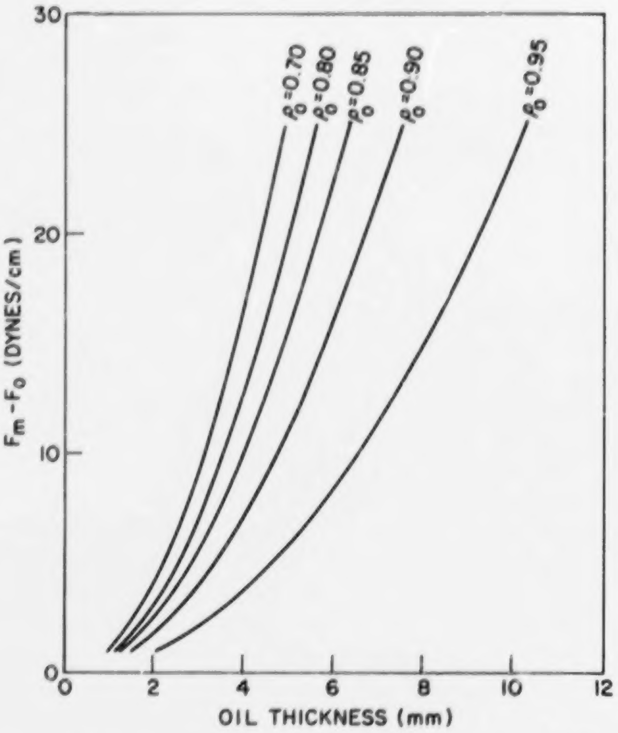


Figure 3. Solutions to Equation (2); spreading pressure difference between the control monolayer and oil ($F_m - F_o$) vs. oil thickness for various oil densities (ρ_o).

TABLE 1. SOURCES AND PROPERTIES OF POTENTIAL PETROLEUM CONTAMINANTS

Type	Source	Density	Spreading Pressure-F_o
Light Refugeo Crude, Texas	Humble Oil Co.	0.84 g/cc	33.0 dynes/cm
Lago Crude, South American	Humble Oil Co.	0.95 g/cc	28.1 dynes/cm
Navy Special Fuel Oil	Cracked Stock, Navy Supply Depot Seattle, Wash.	0.94 g/cc	25.0 dynes/cm
Marine Diesel Fuel	Navy	0.84 g/cc	26.0 dynes/cm
Used Crankcase Oil	NRL Garage	0.91 g/cc	30.5 dynes/cm

Partial source: A Primer on Oil Spill Cleanup, American Petroleum Institute, 20M-12-68.

pressure.[7] In all cases, the velocity of the advancing film front decreased as its distance from the liquid-drop source increased. The movement of slicks and surface films on water bodies follows the motion of the surface water to which the molecules of the surface film are anchored. Of the many physical processes which cause motion of surface water, wind usually is the most influential. The ability of the monolayer to spread against wind is an important factor in the selection of an effective oil control agent. The ability to oppose and spread against the wind also increased with increasing spreading pressure.[7] Thus, materials with high spreading pressure will not only spread most rapidly, but will move against and resist wind to a greater degree than low-pressure surface films.

Oil Thickness Supported by Monolayers

Perhaps the most important limiting parameter relevant to this approach is the thickness of oil which can be supported by a confining monomolecular film. The design of recovery methods used on a confined oil pool will depend upon the oil-layer thickness. If an external spreading pressure is applied by a control monolayer (F_m) it is possible to confine a pollutant oil containing surface-active components with a spreading pressure of F_o as long as F_m is greater than F_o (Figure 2). In this case, the oil lens thickness may be calculated from equation (2).

$$t^2 = \frac{2(F_m - F_o)\,\rho_w}{g\rho_o(\rho_w - \rho_o)} \qquad (2)$$

where t = oil lens thickness

ρ_o = oil density

ρ_w = water density

Oils with densities near that of water are confined in thicker lenses than less dense petroleum products. The lens thickness will also be greater when (F_m) the spreading pressure of the confining monolayer, is high and F_o, the spreading pressure of the spilled oil, is low. Both static and dynamic laboratory tests of equation (2) were performed using a variety of pollutants and confinement films.[7]

The laboratory data compared reasonably well with the expression for oil lens thickness to justify its usefulness. This was particularly encouraging in view of the fact that oil spreading pressures are difficult to measure exactly. Solutions to (2) are shown in Figure 3 where the spreading pressure differential between the oil and control film (F_m F_o) is plotted against oil thickness for selected oil densities (ρ_o). For a particular confinement monolayer whose F_m is known, measurement of F_o and ρ_o can be used in Figure 3 to provide a close estimation of the oil thickness supportable by the monolayer.

Optimum Properties of Control Monolayers

Laboratory studies of spreading rate, wind resistance and oil lens thickness all indicated that control monolayers with a high spreading pressure are most effective. In addition, low oil and water solubility are desirable for monolayer durability on a water surface in contact with an oil spill. The monolayer-forming material should be easily applied to the water to provide rapid, spontaneous, surface coverage.

A chemically unsaturated alcohol, 9-octadecen-1-ol, (oleyl alcohol) has been studied as a useful compound for modifying air/sea interactions and meets most of these requirements. However, its equilibrium spreading pressure, 33.8 dynes per cm on seawater, is only slightly above that of some of the more surface-active petroleum contaminants (Table 1). Promising materials with film pressures in the neighborhood of 40 dynes per cm, which do not interact with alkaline substrates, include the solid saturated fatty alcohols, sorbitan and glycerol esters of fatty acids and the polyoxethylene alkyl ethers.

The solid fatty alcohol monolayers have been utilized extensively for evaporation control, but these materials must be dispensed as finely ground powder or from water emulsions. Their spreading rates from the solid state are quite slow and their monolayers are easily collapsed by wave action into multilayers which do not readily respread. On the other hand, many of the liquid surface-active agents spread rapidly, and their monolayers act like a two-dimensional liquid that will readily respread over a film deficient area caused by breaking water and wave-induced surface dilations.

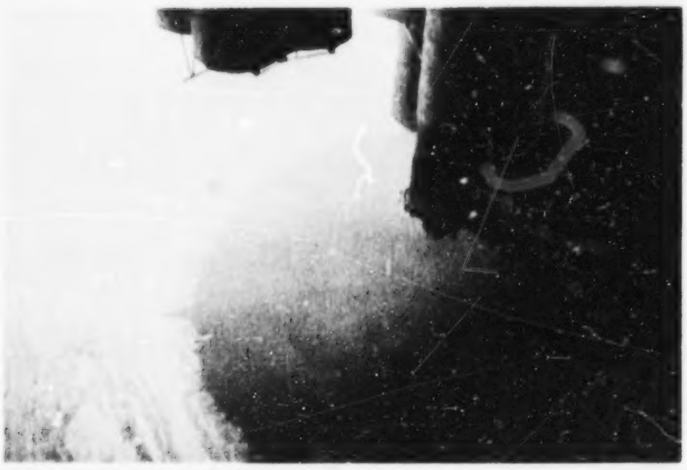


Figure 4. "Hole" in river oil film cleared by one ml. of water-insoluable film-forming agent.

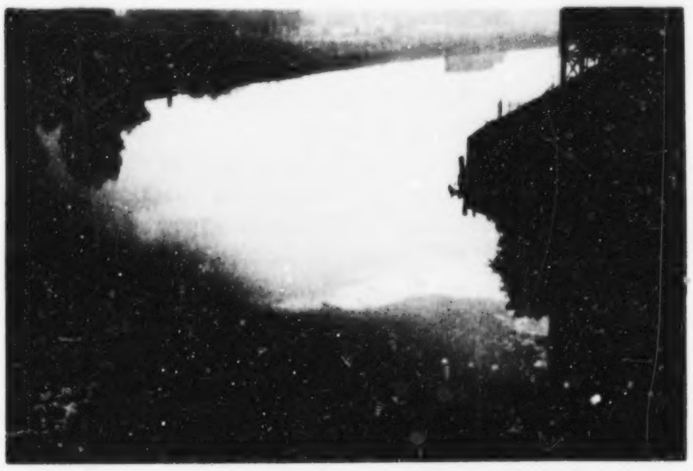


Figure 5. Area of Buffalo River cleared by monomolecular piston film.

Figure 6. Spreading of piston surface film to drive pollutants from vicinity of shore facilities.

Field Evaluations

Several approaches to oil slick control with piston films were tested in October, 1969, on the Buffalo River to determine conditions of usefulness and limitations of the technique. The river runs through the industrial center of the city of Buffalo and is heavily polluted by chemical effluents and petroleum products. This body of water is biologically "dead," contains almost no dissolved oxygen, and much of its surface is covered with a rigid, highly oxidized oil film 0.1 - 1.0 micron in thickness. Oil is also present in emulsified form beneath the water surface and is incorporated in large quantities into the river bottom sediments.

Several commercially available film-forming compounds were investigated which included sorbitan esters of fatty acids and polyoxethylene alkyl ethers. All of the tested materials exert film pressures in excess of 40 dynes/cm and behaved in a similar manner with regard to their ability to drive and contain the surface contamination on the river. However, there were slight differences in the ease of application and effectiveness of the generated piston films between the surface-active agents studied.

The application of small quantities of film-forming agent cleared surface oil and small floating debris from large areas of the river. The initial addition of a milliliter of the surface-active material produced a large cleared hole in the oil film (dark area in Figure 4). The jagged spikes driven into points of weakness in the rigid oil layer are characteristic of the effects of a monomolecular film on a high cross-linked, nearly solid surface film. Shortly after the addition of 10 ml of piston film, a large cleared area developed which grew as it drifted slowly with the surface flow of the river (Figure 5). It was also possible to condense the floating contamination into thickened lenses and scums with a peripheral control film. The condensed pollution could be maintained in this condition by the external film for subsequent retrieval.

The oil-covered river was used as a simulated oil spill which was moving with the surface flow. The piston film was generated along shore in an effort to protect it against the simulated spill (Figure 6) which flowed up river at about two miles per hour. A small addition of the control film drove the moving pollution away from the shore facilities and maintained it at a distance of about 40 feet from the river bank (Figure 7 and 8).

These observations and potential applications are subject to the limitations of surface flow and pollution thickness cited earlier. For example, the piston film was not effective in driving oil several millimeters thick which had accumulated against a floating boom located in Cazenovia Creek near its confluence with the Buffalo River. However, within these limitations, a number of important uses have been demonstrated.

Additional field experiments were performed with freshly dumped oil in the Baltimore Harbor. Five gallons of heavy crude oil was poured onto a water surface area of 5400 sq. feet enclosed by a floating boom, and allowed to spread from the upwind end of the enclosure. The pollutant oil, Jobo crude, was highly viscous, contained 62 per cent asphalt and had a specific gravity of 0.986 g/ml. The Port

Service, a rotating drum skimmer operated by the Maryland Port Authority, was positioned at the opposite end of the enclosed area. The spreading crude oil drifted gradually toward the skimmer until most of the test area was covered with a film of the crude. Ten milliliters of sorbitan mono-oleate was dispensed dropwise along boom at the upwind end. The oil film was rapidly driven toward the skimmer where it was eventually condensed into thick black pools estimated to be 0.5 - 1.0 cm in thickness. The confined pools resembled those formed when the crude oil had first been poured onto the water before it had spread. The cleared area contained no visible oil and was covered only by the monolayer or control agent and a few small lenses of excess unspread surface-active agent. It was also observed that the piston film assisted the operation of the rotating-drum skimmer by providing surface tension gradients to drive the oil toward the rotating cylinders. By maintaining the pollutant in a thick unspread condition which occupied a small area, the mobile skimmer did not have to operate over a large area of water surface.

Conclusions

Surface films whose spreading pressures are 40 dynes per cm or greater, will operate effectively upon oil slicks whose thickness does not exceed 0.5 - 1.0 cm. Thus, it is anticipated that monomolecular piston films will find greatest use against relatively minor spills along coasts or in rivers and harbors. The application of the one-molecule-thick film does not eliminate or disperse surface pollution, but acts as a confining barrier to compress the pollutant into a thick lens and reduce the surface area occupied by the spilled oil. Field studies have demonstrated that the high film pressure monolayers would not move against winds greater than 2m per second.

Although the film effectively compressed the oil into thick lenses, wind-generated surface currents, in addition to the wind drag itself, opposed the upwind spreading of the monolayer. However, the oil was readily confined, condensed and driven from shore when winds were parallel to or away from the point of monolayer application. In open water oil slicks were compressed to small thickened lenses by a peripheral control film. The oil was maintained in a condensed-lens condition even though the oil-monolayer system moved with the surface water flow.

The surface film may be used to confine an oil spill and prevent its further spreading, pending removal or dispersal. Spreading the monolayer between an oil slick and the shore will prevent onshore drift and provide protection of waterfront property until the pollution has moved on to a less vulnerable location, as long as the wind is not onshore. In addition, these films may be useful in driving oil out of inaccessible locations between ships and under docks so that retrieval techniques can be applied.

Acknowledgments

The Buffalo River studies were made possible through the cooperation of the Federal Water Pollution Control Administration, the City of Buffalo and Cornell Aeronautical Laboratory, Inc. The pollution contol experiments in Baltimore Harbor were conducted with assistance from the Maryland Port Authority and the U. S. Coast Guard.

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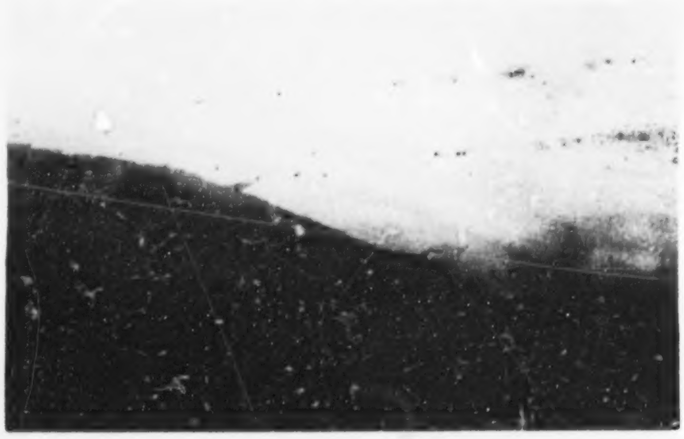

Figure 7. Oily surface pollutants driven from river bank by water-insoluable piston film.

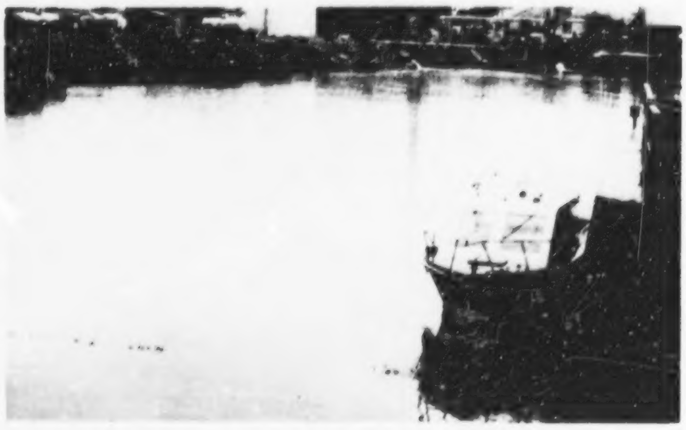

Figure 8. Water front protected from moving oil by piston monolayer.

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New Methods

For Combatting Oil Slicks

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Abstract

A new device has been developed which incorporates the principle of continuous operation for high capacity by means of a floating and circulating absorbent belt. By continuous squeezing of this belt, the oil is separated and the belt can be used over and over again. The apparatus has been shown to operate satisfactorily under practical conditions on inland waters.

Oil slicks at sea can be sunk by means of sand that has been rendered oil-wet by the addition of special wetting agents. This can be accomplished in one fast operation by using a sea-going hopper dredger which first gathers the sand from the sea bottom and stores it still wet in its hoppers. At the site of the oil slick, after fluidisation of the sand with water and a small amount of chemical, the sand/water slurry is sprayed over the floating oil.

This method was shown to have practical potential by large-scale tests with a dredger. Both from an economic and an operational point of view, this seems to be the only potentially viable way of attacking really large oil spills whilst still on the sea.

The problem of removing a floating mass of oil can be tackled in several ways, each technique utilizing a different property of the material in question. Such a technique may be entirely mechanical, for instance skimming by booms and collecting by suction, or it may depend on adsorptive forces as in the case of rotating drums, discs or belts. One proposed method aims at the solidification of the oil layer by jelling in order to facilitate collection, while at the other extreme, that of fine dispersal by emulsification has already been tried on many oil spills. A completely different method of disposal involves burning the floating oil on the water, but this still appears to give rise to serious difficulties.

Two other techniques have recently been under development by staff of the Royal Dutch/Shell Group in the Netherlands, i.e. one based on the absorption of the oil in a porous substance, followed by collection of the saturated absorbent, and the other employing gravity to sink the oil to the bottom after weighting with a suitable material. It is these two modern methods which will be discussed here in more detail.

Absorption

Several materials have been proposed for the purpose of taking up the oil while still on the water surface. One class of these porous materials should be cheap and abundant so that they can be discarded after collection and, for instance, burned with the oil. Many examples of this kind are very simple, e.g. straw and hay, peat and sawdust or tree bark. These materials are successful to a certain extent, but the main problem in their use is the laborious task of collecting them after application.

A more sophisticated class includes such materials as granulated plastic foam or expanded volcanic glass, while rubber powder acts in a different way, i.e. by taking the oil up under swelling. Although these latter substances have stronger absorptive powers than the other cheap materials, they nevertheless suffer from the drawback of being difficult to collect.

One exception must be mentioned here, namely a device employing a drum covered with plastic foam, revolving over the oil-covered surface of the water. In this case the oil is squeezed from the soaked plastic by a roller and the absorbent can be used continuously. However, the capacity of the device is limited by the short contact time available for the absorption and it is also rather vulnerable to wave action.

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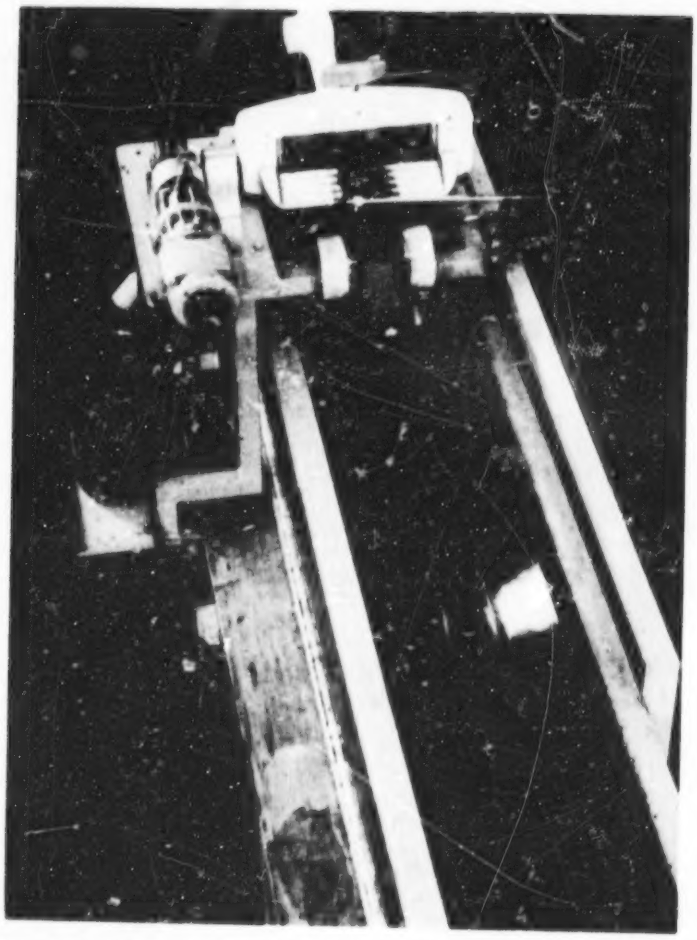

Figure 1. Overhead view of laboratory model for continuous oil removal tests.

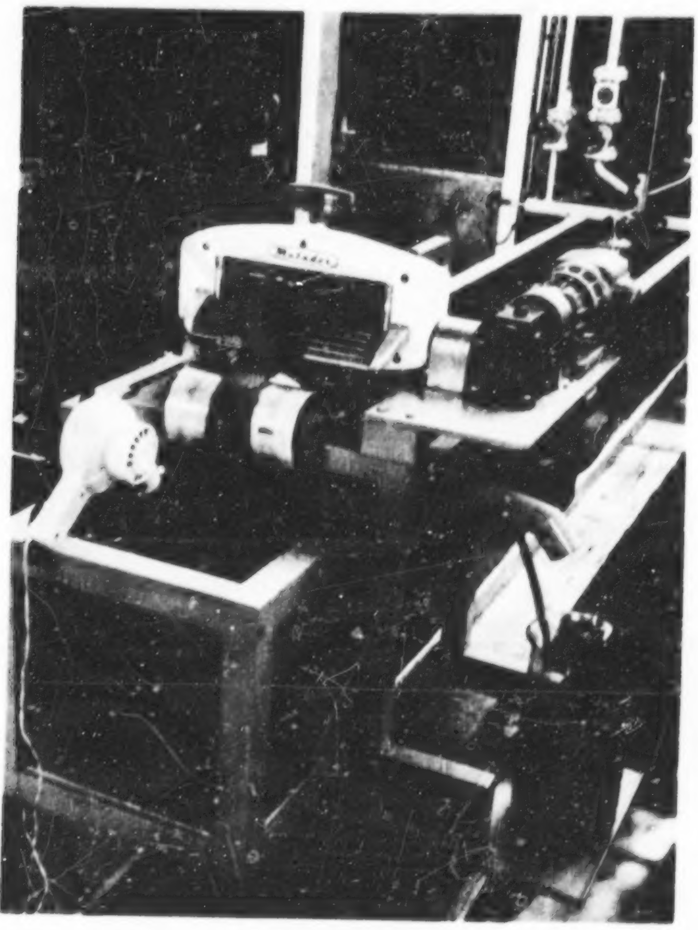

Figure 2. End view of laboratory model for continuous oil removal tests.

Endless Loop

We have attempted to avoid the shortcomings of the methods depending on an absorbent material, realising that a continuous method should be used to remove large quantities of oil. The absorbent material should then take the form of an endless loop, floating freely on the water so as to allow adequate saturation time and then squeezed continuously between rollers to release the oil. After squeezing, the belt could be fed back to the water surface and used again. For this device (called 'oil scrubber'), the material used should satisfy the following requirements:

1. Preferentially *wetted* by oil, so that even in the presence of water only oil can be taken up by capillary suction,
2. Freely *floating* on water so that the absorbing belt will automatically be at the place where the oil is present; the specific weight of the solid material should thus be less than one (gr/cm^3),
3. Durable *resilience* so that the material can withstand frequent squeezing,
4. High *porosity*, making it possible to take up large amounts of oil,
5. The right *permeability*, high enough to enable on the one hand an adequate rate of inflow and outflow of oil during absorption and squeezing; on the other hand low enough to prevent loss of oil by dripping during lifting from the water,
6. *Flexible* enough to follow wave action,
7. High *strength* in order to withstand the tensile stresses during handling and other abuse.

Polypropylene

Laboratory investigations showed initially that a sort of wool of synthetic fibers would be preferable to, for instance, a plastic foam, mainly on the grounds of permeability, resilience and strength. It then became apparent that the only materials lighter than water were polypropylene and polyethylene; moreover, the other synthetic fibers showed inferior wetting properties. Since polyethylene was not available in the required fibrous state, *polypropylene* wool was the chosen material.

There was a choice between spun fiber and fibrillated sheet. The latter showed superior properties and was therefore selected.

As regards the construction of the belt, a tube-shape was first used, consisting of a strong skin of nylon or terylene stuffed with polypropylene wool. Later a flat belt type was preferred, since this runs better between the rollers and can be manufactured mechanically from polypropylene felt, obtained from the fibrillated sheet material by needling.

Laboratory Model

When the most favourable conditons had been established batch-wise, a small continuously operating laboratory model was constructed (see Figures 1 and 2). This model uses belts of about 5m length and up to 10cm width; squeezing is performed by an ordinary washing wringer. The model not only proves that the principle of continuous removal by means of an endless loop is workable, but it also serves to demonstrate how remarkably quickly floating oil can be removed with such a simple arrangement: the capacity proved to be of the order of 10 tons of oil per day.

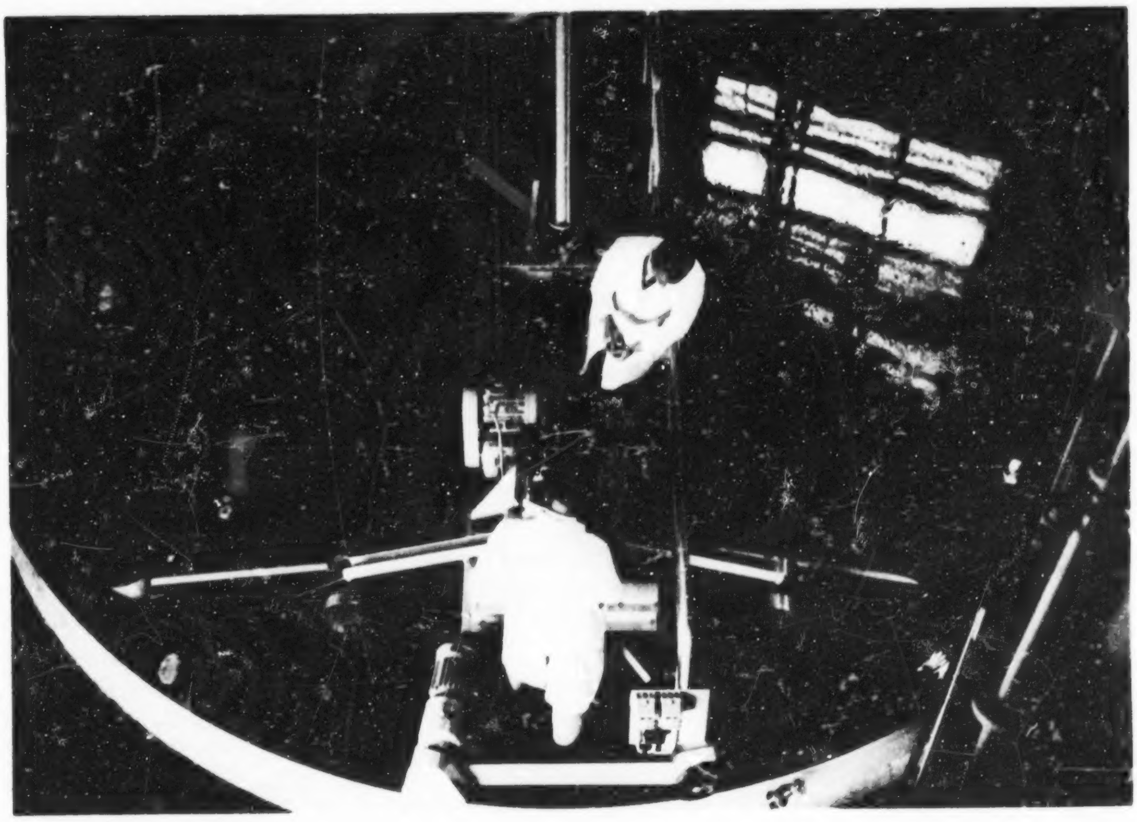

Figure 3.
Pilot installation for continuous oil-slick removal experiments.

Pilot Model

The next step was an enlarged, pilot-scale model, employing a continuous belt of 20m length and up to 30cm in width (see Figure 3). By nature of its special construction with the squeezer rollers on a rotatable bridge over a circular basin (7m diameter), another variable can be introduced, namely that of dragging the belt sideways over the surface of the water.

In this model the effects of circulation speed, oil-layer thickness and oil viscosity were investigated. The test results indicated that under conditions of plentiful oil supply, the removal capacity would be up to 80m^3/day.

One limiting factor of the present method is that it is restricted to oils with viscosities up to 300cS. At higher values, the rate of absorption becomes low and the belt slips between the rollers because of the excessive pressure required for squeezing.

Encouraged by the equally smooth operation of the large model, it was tried out in Pernis petroleum harbour (see Figure 4). No special difficulties were encountered with a 40m belt, and even under conditions of polluted water and floating debris, the polypropylene belt removed the oil at a rate of up to 30m^3/day.

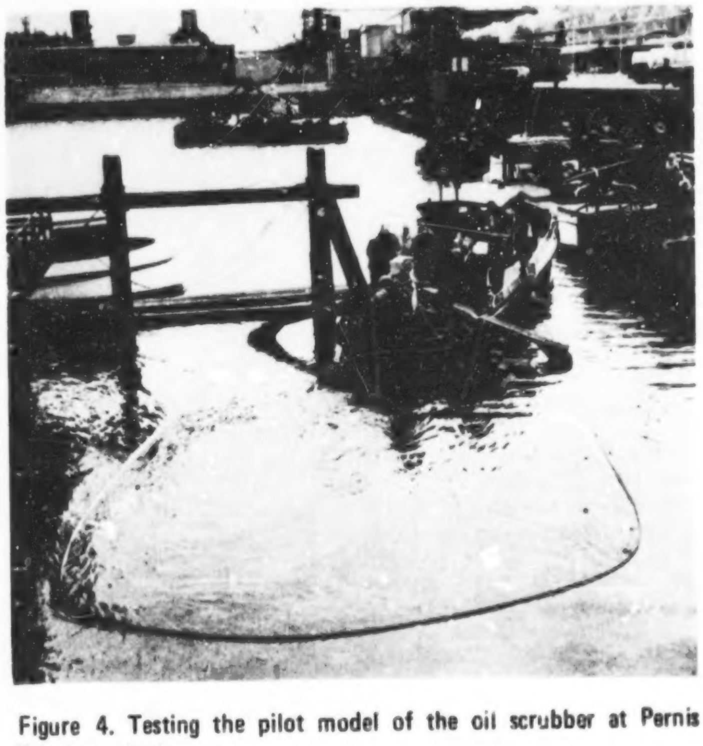

Figure 4. Testing the pilot model of the oil scrubber at Pernis Petroleum harbor.

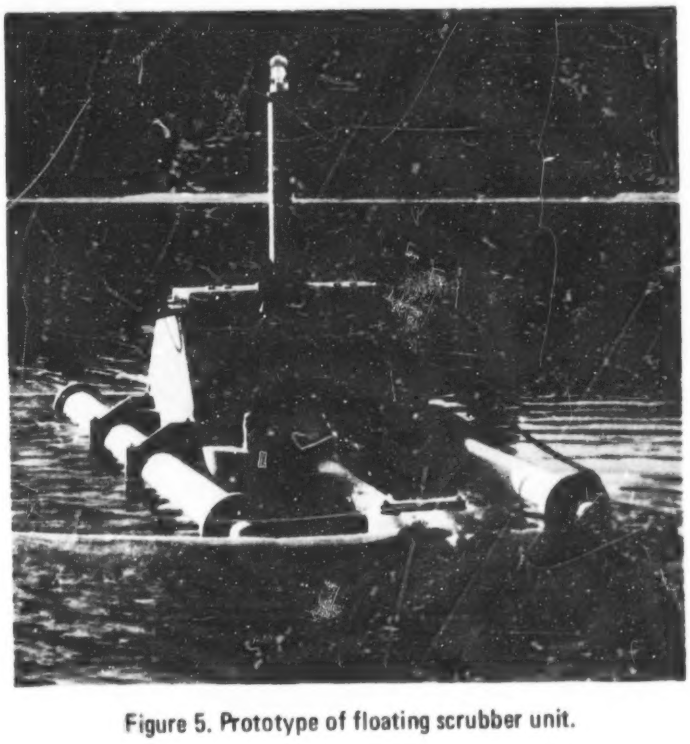

Figure 5. Prototype of floating scrubber unit.

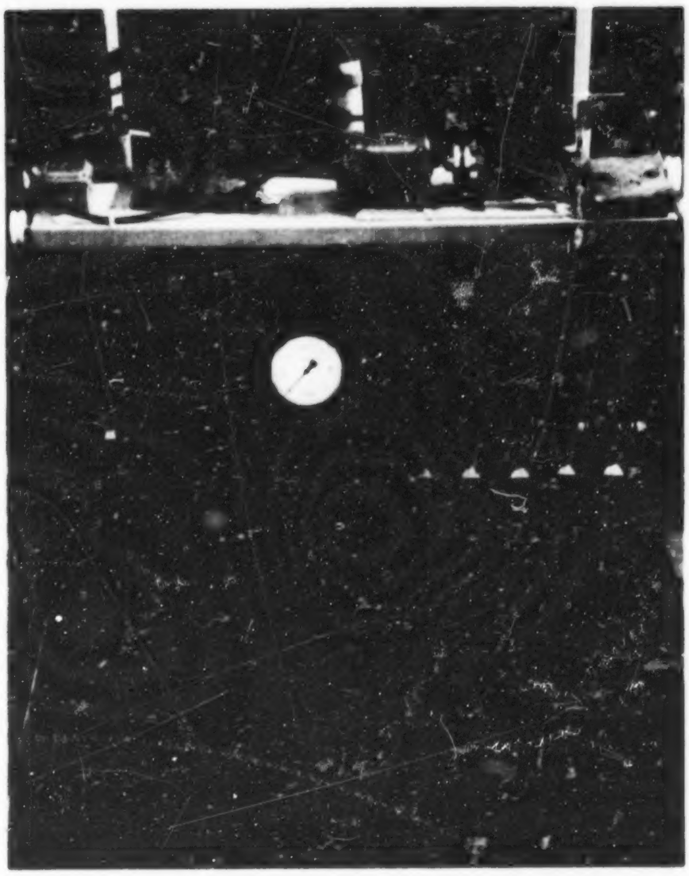

Figure 6. A slick of viscous oil, 5 mm thick, in the test tank.

Floating Unit

As the next step towards application, a prototype of a completely independent and mobile unit has been constructed (see Figure 5). This unit comprises an electrically driven floating squeezer provided with an electrical oil pump to transfer the squeezed-out oil from the sump under the rollers to a tank. Electrical power is provided by cable from a diesel-powered generator on shore (or on a barge); the drive, etc. is remote-controlled. The whole unit can be easily transported by truck, ship or even by plane to the site of an oil spill. Because of the floating arrangement of the squeezer and the flexibility of the long absorbent belt, the latter can be maneuvered into any tight corner or shallow spot for removal of the last oil spots.

Sinking the Oil

Although several methods for oil removal have been successfully applied on a relatively small scale and under quiet conditions, no practical method appears to exist for combatting large oil slicks (of at least several thousands of tons) at sea. It was suggested that if none of the other methods worked, sinking the oil to the bottom of the sea would be acceptable as a rough but ready method.

Weighting of the oil with a heavy powder had already been mentioned, but laboratory experiments soon showed that the various materials readily available in bulk behave differently when sprinkled onto floating oil. Several of the cheap, abundant materials such as sand, chalk, cement or bentonite may sink the oil for a short time, but the water

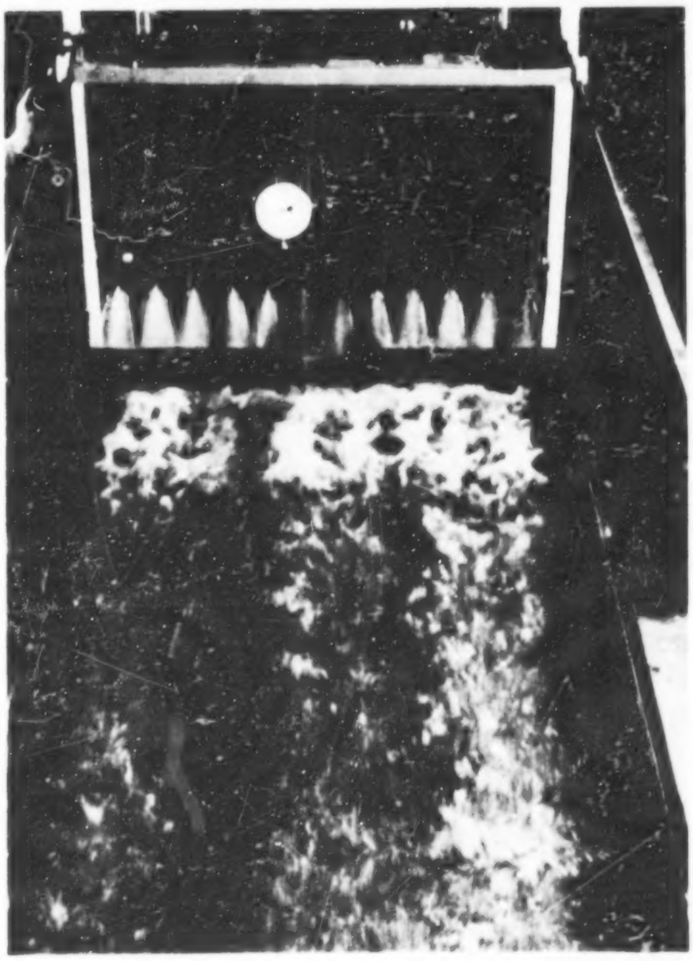

Figure 7. The oil shown in Figure 6. is treated with an oleophilic sand/water slurry.

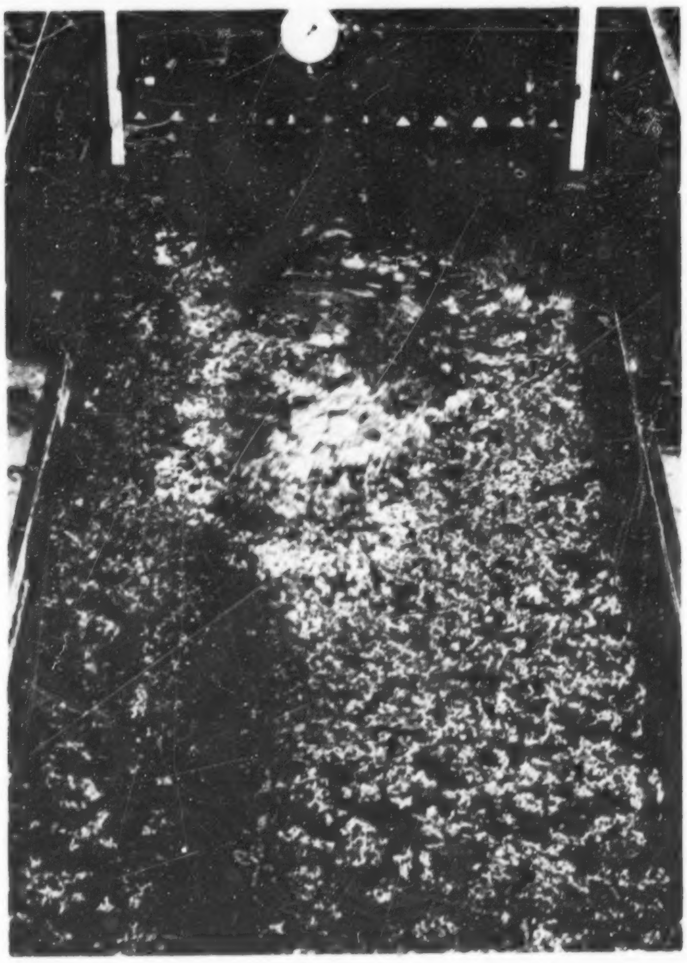

Figure 8. Following treatment shown in Figure 7. the oil slick was sunk to a large extent by the slurry.

soon replaces it from the sunken conglomerate and the oil reappears at the surface.

Other powders, such as sulphur, talcum or slag seem to sink the oil more permanently. It is the *wetting character* of the material that is the decisive factor. If the particles are water-wet by nature (e.g. sand), the oil cannot stick to the surface of the grains permanently; if, on the other hand, the material is wetted by oil, the latter cannot be replaced from it by water.

In one case at least, the wetting properties of a cheap, naturally occurring material have been changed deliberately: the surface of chalk particles can be coated with a stearate-film which makes them so water repellent that they remain floating on water until they come into contact with oil. If the oil has absorbed enough chalk, the mass becomes heavier than water and sinks. There seems to be no doubt that the sunken conglomerate is very stable, and this method has been applied repeatedly off the French coast. It is difficult to obtain reliable estimates of the amounts of stearated chalk required; moreover, spreading of the extremely light and fluffy powder in windy weather is extremely difficult.

Even if a cheap and effective oleophilic powder were available, special methods of storage, handling and spreading would have to be developed, and for large-scale application in case of serious disasters, expensive specialized ships would need to be readily available. However, these drawbacks could be overcome if normally water-wet but readily available *sand* could be turned oil-wet in a simple way.

Treating Sand

Treatment with stearate (like the French chalk) does not work in this case. Treatment with silane vapours, while very effective, is extremely expensive and cumbersome. Coating with paraffin wax is another possibility but an equally impractical one. However, numerous wetting agents are being used in the industry as coupling agents. These substances (mainly different amines) work even in watery solutions, and as such, need only to be added to a sand/water slurry in order to turn this sand oleophilic.

Sand Slurry

The remainder of the problem, that of handling and transportation, can be solved now that sand may be used as a slurry in water. A number of sea-going trailer hopper dredgers exist that are capable of dredging pure sand from the sea bottom, storing the wet sand in their holds and steaming to the site of the oil slick. There the sand can be fluidised with water and the chemical added, after which the mixture can be sprayed over the floating oil via the dredger's own powerful pumps. Of course by the time the method may have become operational all necessary steps will have been taken to ensure that no unacceptable side-effects will occur.

The different phases of this envisaged process were first studied in the laboratory. The numerous wetting agents on the market were first screened on their ability to render sand oil-wet, by means of a simple shaking test. It appeared that the most effective ones (e.g. Armour's Armac-T or Duomeen-C) are adequately active in ratios of 0.1%w on sand.

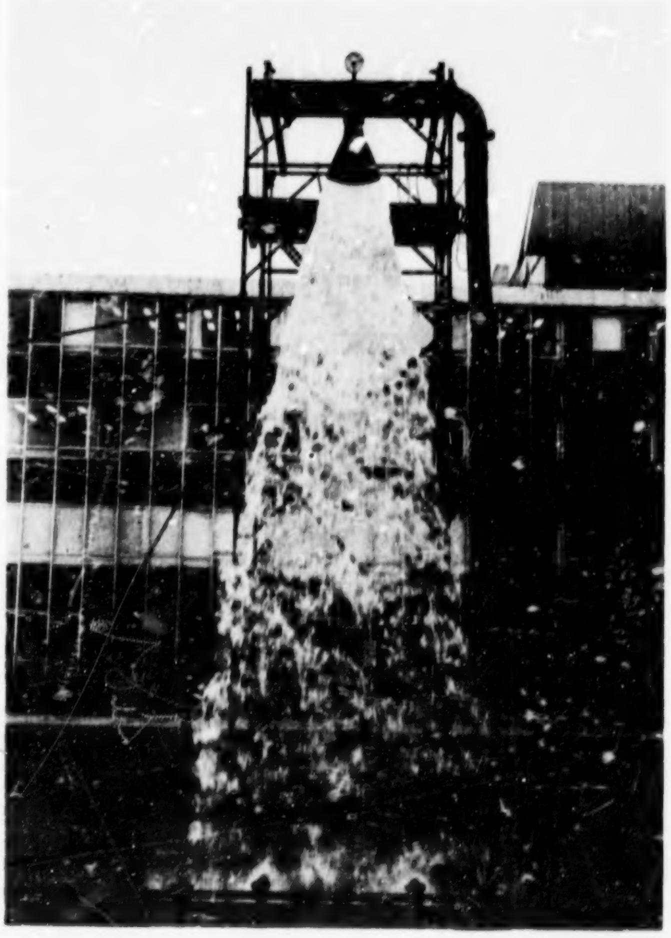

Figure 9. Front view of full scale test of spray nozzles.

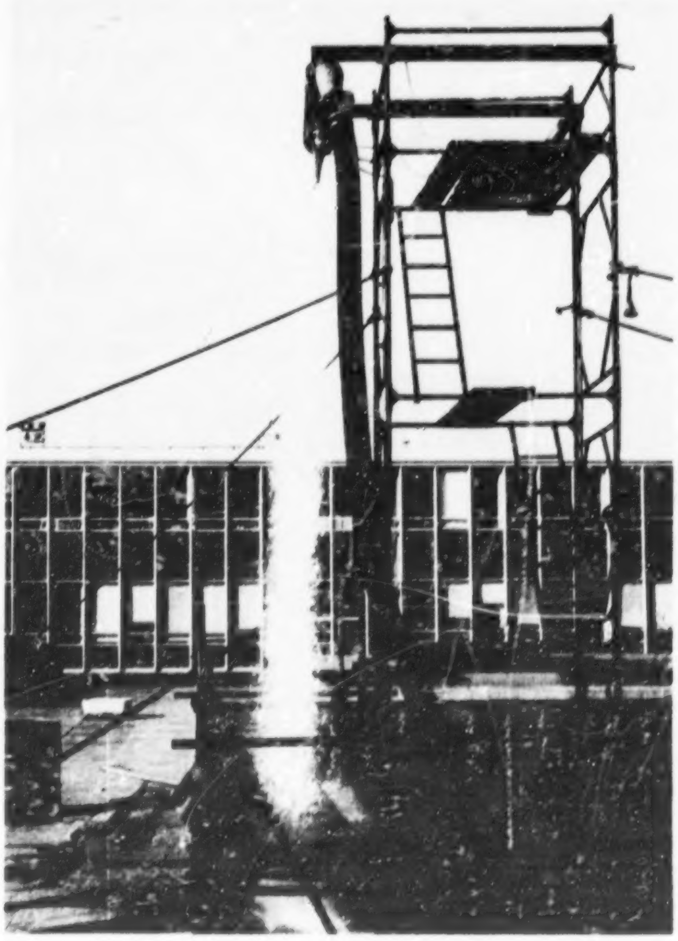

Figure 10. Side view of nozzle test.

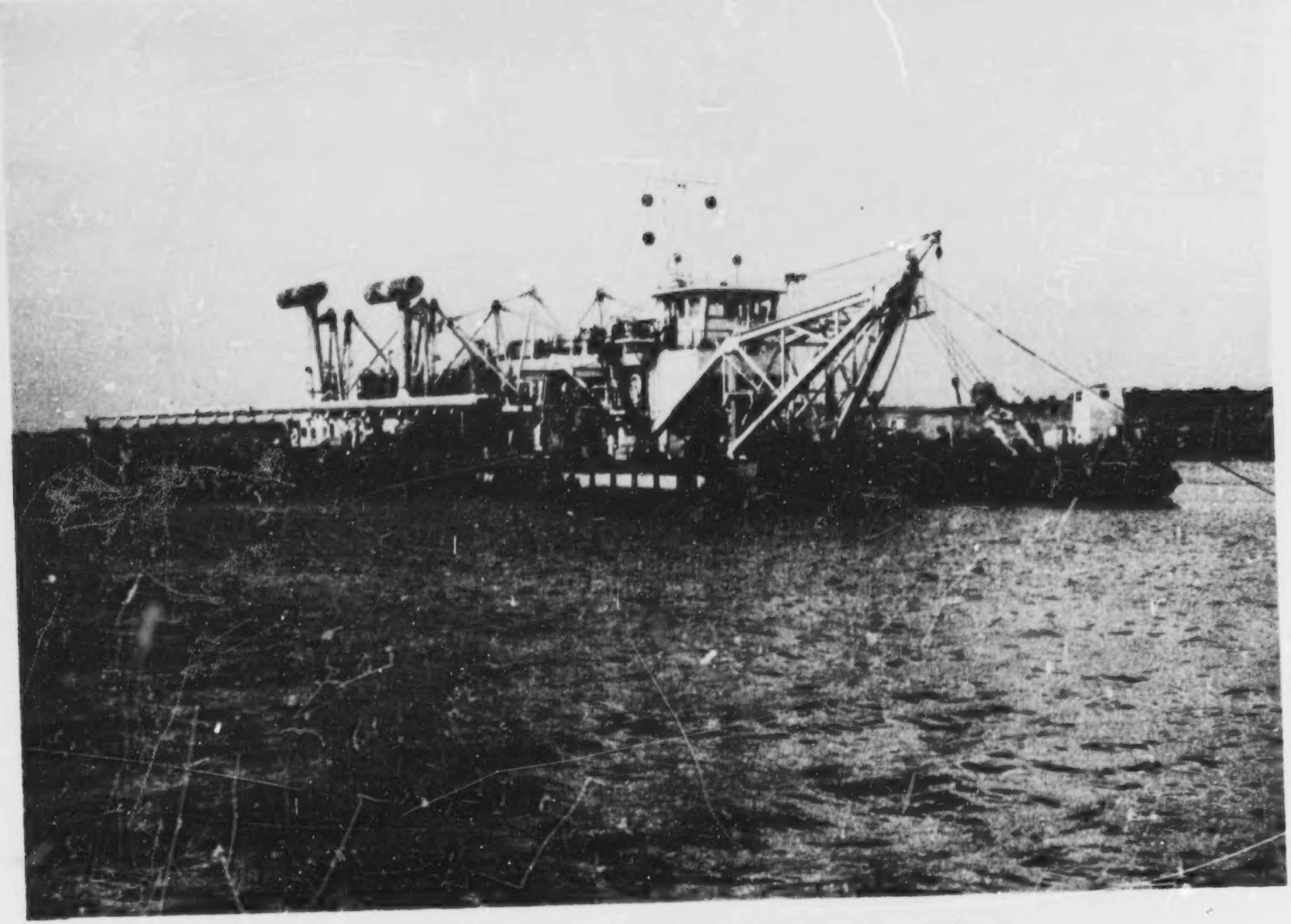

Figure 11. View of large scale spraying boom installed on a suction dredger.

Spraying Tests

The most promising agents were then tried out in small-scale spraying tests. A spraying boom with nozzles giving a flat curtain of spray was passed over a tank (1½ x 3½m) filled with sea water and oil (see Figures 6, 7 and 8). Sand/water slurries are thus spread over the floating oil and variables such as chemical concentration, slurry weight, speed and oil-layer thickness can be studied. It appeared that using a 1:1 weight ratio of sand/oil, a 5mm layer of heavy crude could be permanently sunk with an efficiency of 96%.

However, this method also has a limitation in that the viscosity of the oil that can be sunk successfully should not be too low, the lower limit probably lying around 200cS (at sea temperature). In this respect, the sand sinker method and the polypropylene scrubber complement each other very well.

Another item to which considerable attention was paid was the shape of the nozzles. Since scaling rules were not considered sufficiently reliable for this type of slurry flow, these tests had to be performed full scale, i.e. at pumping rates of 300m^3/hr and from heights of 4 to 5m (see Figures 9 and 10).

Large-Scale Test

At the same time as this development work was being carried out, preparations were also being made for a large-scale test on an actual dredger. To this end a boom was designed, carrying 20 nozzles at intervals of 1m (see Figure 11). The boom was mounted on one of the discharge pipes of a suction dredger, operating in the new harbor of Europort. This stationary-type dredger has no hopper for sand storage, but discharges the dredged slurry straight into open barges for disposal elsewhere. Facilities for injection of the wetting chemical were installed on the main pumping pipe.

Since it was obviously wise to avoid contamination of the harbor by oil, open barges were filled with water with a layer of oil on top. These barges could be towed at a predetermined speed under the stationary spraying boom, thus simulating the effect of a boom on a steaming dredger passing through an oil slick (see Figure 12).

During August of this year, a series of tests were run using this arrangement, and the method was demonstrated to representatives of interested authorities from the Netherlands, Great Britain, Belgium, France, Germany and the United States. It was shown that the scheme is workable and that the variables chosen were of the correct magni-

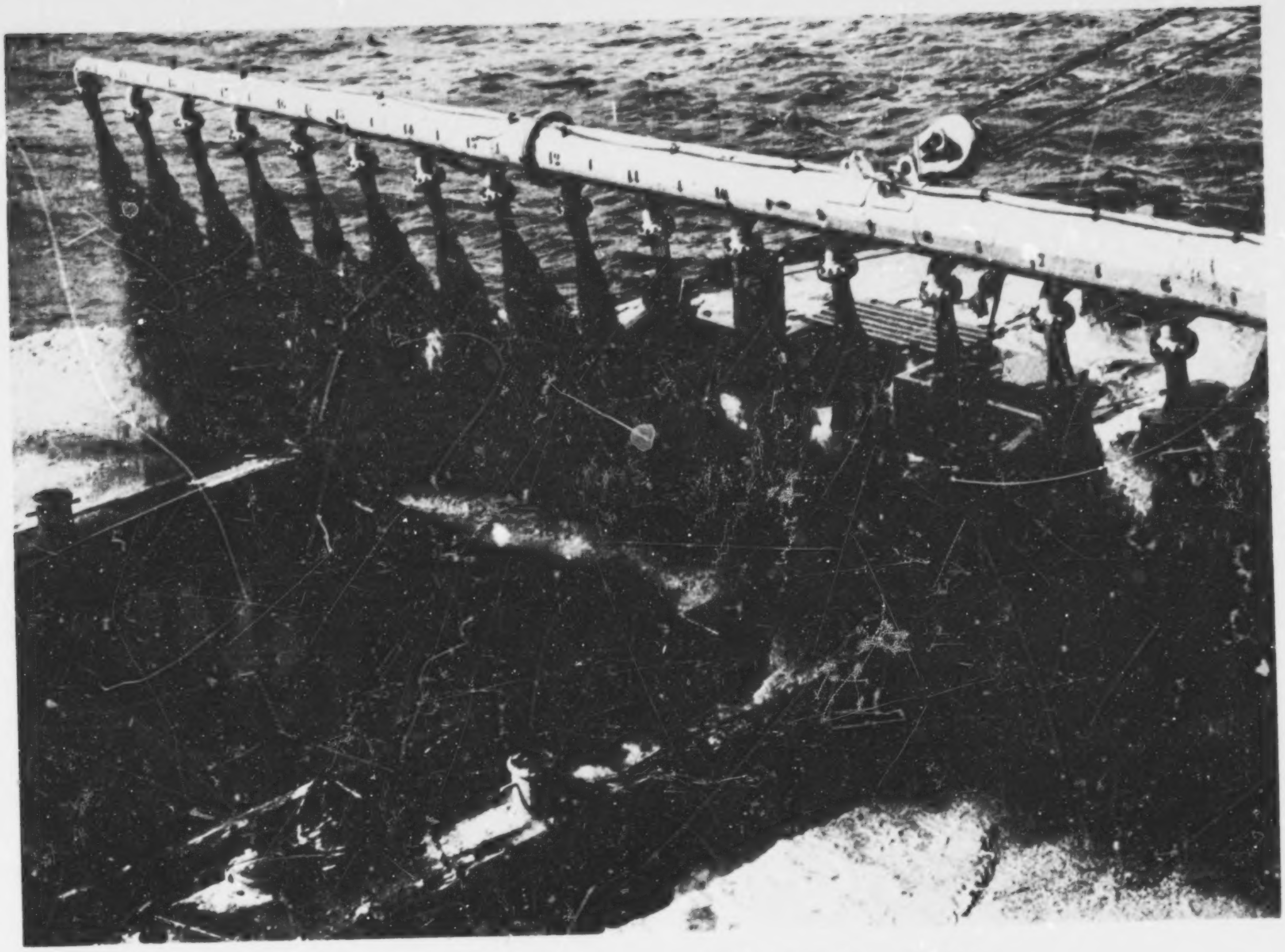

Figure 12. Barge with floating oil passing under the large scale spraying boom.

tude. A flow of slurry of 6000m^3/hr was applied over a width of 20m, thus discharging sand at the rate of 1500tons/hr. For a speed of 5 km/hr and an oil-layer thickness of 12mm, this amounts to a sand/oil ratio of 1.25:1.

One unforseen drawback was the fact that the dredged material from the bottom of the harbor to be deepened appeared to contain an unusual amount of fines (clay). It was known that the presence of clay would have an adverse effect on the efficiency of the performance, because this fine material absorbs the wetting agent. Notwithstanding, the presence of up to 20 per cent of clay in several of the runs, the percentage of oil sunk was still reasonable. A typical figure might be 75 per cent sunk at 10 per cent clay content.

A clear correlation was obtained between clay content and performance, as measured by the percentage of oil sunk (see Figure 13). This means that with sands containing less than 1 per cent clay, an efficiency of considerably more than 90 per cent can be expected, corroborating test results in the laboratory.

Full-Scale Trial

It is well known that on the bottom of the North Sea and the Channel the sand is very pure. This means that in an actual operation when sand is taken from the sea bottom, high efficiencies can be expected.

A trial of a suitable and deliberately laid oil slick at sea is planned in the very near future. If this trial proves successful, it is envisaged that contractual arrangements could be shortly concluded in order to render the Shell Sinker Method fully operational for emergency action in the North Sea and English Channel areas.

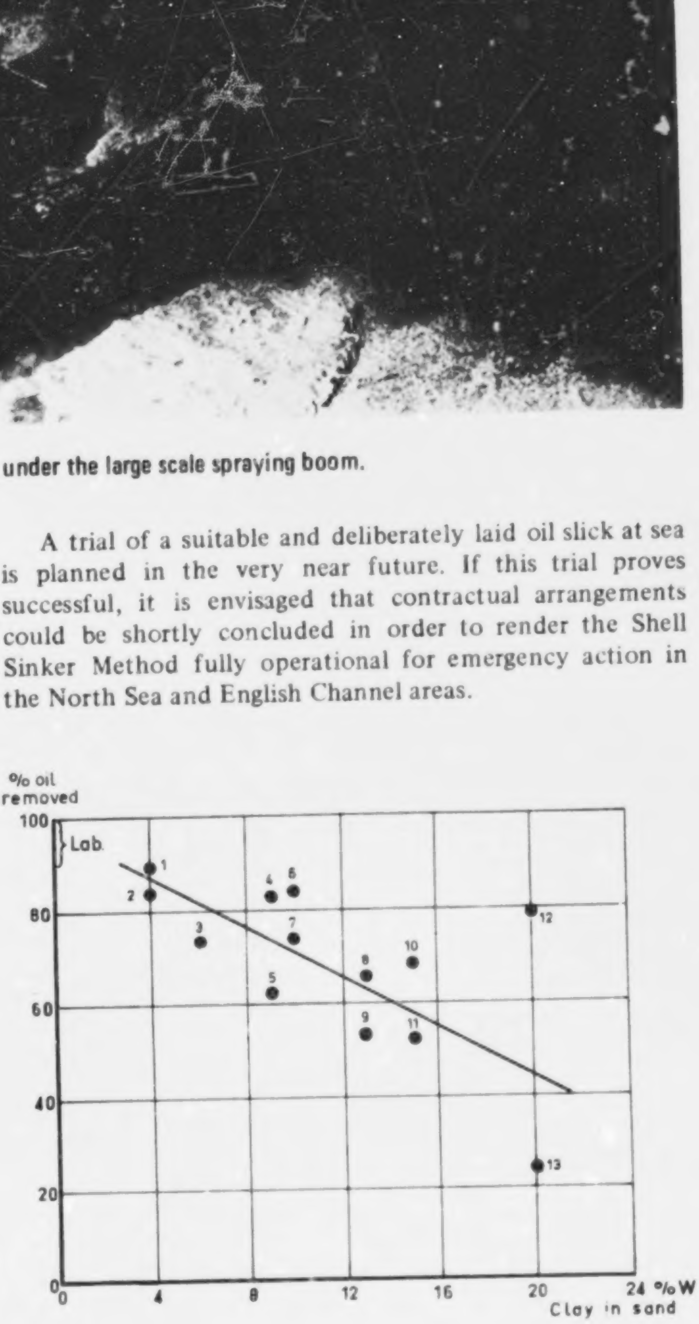

Figure 13. Graph showing the relationship of various sand/clay mixtures and per cent of oil removed by these mixtures.

Pollution Control At A Major Oil Spill

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Abstract

The eruption of crude oil from the ocean floor five and one-half miles offshore from Santa Barbara, California on January 28, 1969, created a substantial task of pollution control and property cleanup. In spite of all difficulties encountered, the beaches, harbors, houses, boats and shoreline have been restored, and in some cases, exceed their original beauty and cleanliness. The cleanup has been costly and time-consuming. More than $4,500,000 has been spent in the prevention of pollution and restoration of property and the environment.

On January 28, 1969, at about 11:00 a.m. during and following normal well drilling operations at Union Oil Company's Platform A (lease 402) in Federal waters off Santa Barbara, California, an oil leak occurred. Federal and State regulatory agencies were promptly notified and company executives and management personnel were alerted.

Observations made at 7:30 a.m. on January 29, in an over-flight of the area by helicopter, showed a major, violently agitated area about 800 feet east of Platform A. A brownish appearing mixture was erupting from the water surface, spreading in a circular configuration. The shade of the mixture darkened with distance from the source, taking on a more typical appearance of crude petroleum about three-quarters of a mile from the emission. Several small emissions were observable along a west to east line, with one small emission west of the platform. The densest area was about one-half mile in diameter and involved the platform structure. An oil slick approximately 25 square miles in area extended easterly from the platform. Patches of oil were breaking off from the main body in wind rows. These patches were tending toward the Santa Barbara, Montecito, Summerland and Carpinteria beaches.

Phase I–Efforts to Limit Pollution

The first pollution control objective was to disperse, with chemicals, the smaller oil patches headed for the beaches until such time as containment and recovery equipment could be marshalled to attack the main oil slick.

Simultaneously, an organization had to be established and manpower mobilized. In this respect, it must be noted that the assigned Union Oil Company Oil and Gas Division personnel had their hands full, working on stopping the oil source. Needed personnel, especially supervisors, were obtained from other divisions of the company, particularly from the Refining Department.

Because of widely circulated reports of damage resulting from the dispersants used by the British in their battle with the oil from the *Torrey Canyon* wreck, many public water pollution control agencies either objected to, or forbid their use.

In order that all misunderstanding could be avoided, request was made and permission received at 3:30 p.m. on January 29 from Washington, D. C. via the Regional Office of the Federal Water Pollution Control Administration, to use chemical dispersants. Use was to be in accordance with Department of the Interior policy on the use of chemicals to treat floating oils as follows:

1. Chemicals should not be used to emulsify, disperse, solubilize, or precipitate oil whenever the protection or preservation of the following are of concern: (a) fresh water supply sources, (b) major shellfish or fin fish nurseries, harvesting grounds or passage areas, (c) beaches.

Such chemicals should only be used in those surface water areas and under those circumstances where preser-

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vation and protection of water related natural resources is judged not to be the highest priority, or where a choice as to resource preservation may make the use of such materials a necessary alternative.

2. Examples of areas and circumstances where the use of such chemicals might be acceptable are:
    a. Where fire or safety hazards are presented by the spill of a petroleum product;
    b. Where large numbers of waterfowl may perish because of the proximity of floating oil;
    c. Under certain conditions, as a "polishing" or final clean-up of light slicks of oil following mechanical removal of floating oils.
3. Chemicals that emulsify, disperse, solubilize or precipitate oil should be used only under the immediate supervision of the Federal Water Pollution Control Administration except where it is judged that fire or safety hazards require the immediate application of such chemicals.
4. When chemical compounds are used in connection with oil clean-up, only those compounds exhibiting minimum toxicity toward the aquatic flora and fauna should be used. The Federal Water Pollution Control Administration is now developing and will soon issue a standard procedure for determining the toxicity of such chemicals.
5. Materials which aid in the collection of floating oils such as sorbents, gellants and viscosity control additives are considered to be generally acceptable providing that these materials do not in themselves, or in combination with the oil, increase the pollution hazard.
6. Research and development to improve chemicals which emulsify, disperse, solubilize or precipitate oil is encouraged. Whenever it is demonstrated to the complete satisfaction of the Federal Water Pollution Control Administration that such a chemical, by itself and in combination with oil, is non-toxic, its use may be approved in the areas where the protection or preservation of a. fresh water supply sources, or b. major shellfish or fin fish nurseries, harvesting grounds or passage areas are a prime concern.

A work boat whose fire water pump had been adapted for applying chemical solutions was dispatched to Platform A to disperse the oil and gas now presenting a substantial fire hazard to the structure. A small supply of Guardian Chemical Company's Polycomplex A-11 was on hand and was used this first day.

Two crop dusting airplanes and a supply of Enjay Chemical Company's Corexit 7664 were hurriedly ordered and ready for use January 30. The decision to use Corexit 7664 was based on reports of its low toxicity to marine life and reports of its successful dispersion of oil from a large tanker spill. Some comparative bioassay data are shown in Table 1. The chemical company representatives were on the scene to supervise the use of the chemical and assist in the operation.

The dispersant was applied by the airplanes on January 30. Application was at a rate of 40 gallons/acre, using full concentration (40% active material).

No dispersants were used inside the one-mile limit at any time, except on the evening of February 4, when oil penetrated the Santa Barbara Marina.

Efficient application of the liquid dispersant was not good due to the problem of locating the oil patches from low-flying aircraft. The procedure was to locate a slick visible from an altitude of perhaps 1000 feet, then circle back and spray the slick from an altitude of about 50 feet. At best, only an approximate location for the chemical drop could be made.

On January 31, the application of dispersant was carried out by both airplane and boat. The two crop dusters worked on isolated slicks, migrating toward the beaches. A specially equipped spray boat worked on the shore side edge of the main slick and the original work boat, using a pump, hose and nozzle, dispersed the oil under and near the platform.

By the evening of January 31, an inventory of 125 drums of Corexit was on hand and an additional 120 drums in transit. A total of 147 drums (8085 gallons) had been used the first two days. Work was in progress to equip two additional boats for chemical application. Assignments for an all-out effort to disperse slicks, some within two miles of the beaches, were prepared the night of January 31 and early morning hours of February 1.

A survey of the Santa Barbara Channel at dawn February 1, revealed the oil slick thickly packed in approximately a one-mile isosceles triangle whose apex was Platform A. The slick thinned out in a southeasterly direction with a show of dense patches as far east as Rincon Point, approximately 15 miles away. A thin, grey film covered an area of about 150 square miles.

The aircraft were readied for takeoff and the spray boat dispatched to a point two and one-half miles offshore from Summerland, where a dense patch of oil had been located. At 8:30 a.m., the Regional Director of the Federal Water Pollution Control Administration requested cessation of all uses of chemical dispersants.

The Director was of the opinion that based on the manufacturer's claim of 50 gallons of oil dispersed per gallon of Corexit applied, 10,000 barrels of oil should have been dispersed. Since the Company estimated the emission at 500 barrels per day, obviously the dispersant was ineffective. This conclusion upon examination was not valid, since there was no way of determining the efficiency of application. The important question was the effect on the marine ecology due to the concentration of the dispersant in the water column. The concentration was variously estimated at less than one part per million. Nevertheless, all chemical use was discontinued, airplane orders were cancelled and boats programmed for spraying were diverted to other uses.

At 3:00 p.m., the Federal Water Pollution Control Administration (FWPCA) order was rescinded and permission was given to continue to protect the platform with dispersants and to use them on the leading shore edges of the slicks, in choppy water outside the one-mile limit. However, the main thrust of the chemical treatment has been blunted and although additional spray boats were later used, airplane application was not again attempted.

Concurrently with the chemical treatment, a program for containment and removal of the main slick was formulated. A reinforced inflated plastic boom had been recommended by the Union Oil Company Research Department. A 1500-foot boom to be delivered in 500-foot sections, one each on February 1, 2 and 3, was ordered. The boom had a cross section diameter of 20 inches and was equipped with a 30-inch skirt, weighted with sand.

A floating skimmer for pumping oil from the water surface was under construction. A boat equipped with pumps and piping was being readied for use with the skimmer.

It was planned to concentrate on large sections of the oil slick with the boom, and pick up the oil with the skimmer, using a work boat's water tank for storage. A modification of this system worked well later in the emergency.

Other work boats, harbor booms, a barge and pumping equipment were located and leased.

No significant beach involvement with oil had been observed or reported up to February 2, 1969. All marinas and harbors proximately threatened had been equipped with booms and staffed with boom watches. A wildfowl treatment center had been established and staffed at Carpinteria Beach State Park to clean and house birds, now being affected in substantial numbers.

By February 2, the wind rows of oil and oil patches were, in some sections, within one mile of the seashore. It had been observed that there was a natural current barrier along which sea grass, storm trash and other debris had collected. This natural barrier extended from Santa Barbara to Oxnard at varying distances from the shoreline. At places, oil was collecting along the barrier. It was decided to attempt to reinforce this natural barrier with straw along those sections approached by the oil slick.

Straw mulchers used by the California Division of Highways to protect fill areas from water erosion were located through the assistance of the California Disaster Committee and the California Highway Patrol. These machines capable of broadcasting eight to 10 tons of straw per hour were delivered and put in service, one each on February 3, 4 and 5. A straw supply was obtained through the Union Oil Company Purchasing Department, the owners of the mulchers and local suppliers. Shipments were received from as far as Arizona.

The first section of the plastic boom did not arrive until late February 2. Crews worked all night to inflate and assemble this section. By daylight February 3, it became apparent that the boom would not meet open sea requirements. The sand used for weighting the skirts, migrated and caused boom sections to jack-knife, leaving breaches in the boom. Fittings broke under tow and sea stresses. It was decided to build log-type booms as a substitute.

A supply of wooden pilings was located in Los Angeles and the Guy F. Atkinson Co. was hired to build two, two thousand foot long wooden booms. The pilings were connected with one-inch steel cables. A seven-eighths steel cable, extending the entire length of each boom, was installed for towing and anchoring.

By 7:00 p.m. February 3, crews, equipment and materials had been assembled at Santa Barbara. The booms were finished and ready for use 20 hours later.

The staging area, by this time, has been described by some Pacific service veterans as reminiscent of the drive and vigor of a landing operation. There was an extreme sense of urgency felt by all of the oil industry personnel and their contractors. Hours of work and energy expended, ended only when near exhaustion.

The oil containment and recovery plan called for the Coast Guard to supply five pontoons as platforms for pumping and oil skimming equipment attached at the apex of a triangle formed by the wooden booms. The Coast Guard was to provide the anchoring system and boom tending operation.

The booms were turned over to the Coast Guard the afternoon of February 4, as scheduled. Because of heavy seas, they were able to tow only one of the booms to the platform and it subsequently broke away, with one 900-foot fragment returned to Santa Barbara harbor that night by the Coast Guard. The second boom was beached by Union Oil Company contractors when the Coast Guard could not handle it at sea.

Two of the five pontoons broke away under tow and went ashore near the Biltmore Hotel. The remaining three were tied up at Stearns wharf, Santa Barbara. The forces of the sea were vividly demonstrated that night.

The storm of February 4 and 5 completely scattered the oil slick. Beaches were covered with oil. High tides and strong winds sprayed sea walls, cliffs and homes with oil. It was a dismal picture that greeted the viewer on February 6.

Because protection of the beaches was now redundant, use of chemical dispersants was discontinued on February 6, except for fire mitigation in the immediate vicinity of the platform and were not again used in any significant amounts until February 25.

On March 4, 1969 the U.S. Geological Survey extended the use of chemical dispersants outside of the immediate platform area (one mile circle) for dispersal of oil slicks. The following criteria promulgated in accordance with the National Multi-agency Pollution Contingency Plan.

1. Dispersants are not to be used unless all efforts possible are made to boom, contain, and *collect* such oil in the immediate vicinity of the platform.
2. All dispersant application is to be conducted under supervision of company staff and directed by competent company aerial surveillance. Government observers are to be allowed to observe and sample whenever they deem it necessary.
3. Only water soluble, non-aromatic, non-toxic (in dosages used), dispersants of proven effectiveness are to be used. No more than three different materials may be used at any one time. Application

of each of these materials shall be in distinctly different areas so that interaction between different materials shall be minimized.

4. Dosages shall be limited to no more than 5 ppm of the material when applied, calculated on the basis of mixing in a water column of three feet depth, multiplied by the width of the area of actual spraying, including the wake of the vessel, and multiplied by the distance traveled.
5. No material is to be dispensed except onto oil slick areas.
6. No application of chemicals is to be made in the waters of the State of California (within three miles of shore).
7. All application shall be in accordance with the best practices to obtain adequate mixing and dispersion.
8. A daily record of dispersant use is to be maintained by the company as to volume, product, vessel, and rate of use and the daily record furnished to the FWPCA.

No endorsement by the U.S. Government of the effectiveness of any product used, nor liability for its use is implied by this concurrence. The use by the company of dispersant materials shall be on the express condition that the U.S. Government, its officers, employees and agents, shall not be responsible for any damages or losses of whatsoever kind or nature, resulting from the company's use of the chemical dispersants, and the company shall agree to indemnify and hold harmless the United States, its officers, employees and agents for all such damages or losses.

To determine the dispersants that may meet the criteria of Item 3 above, toxicity should be measured by use of standard bioassay procedures, using marine organisms common to the area. Samples of the materials used shall be made available to FWPCA when requested.

This concurrence is under Paragraph 2b of the "Department of the Interior, Federal Water Pollution Control Administration Policy on the Use of Chemicals to Treat Floating Oils," July 5, 1968. A previous concurrence under Paragraph 2a of the Policy shall continue in effect at such times as there is a fire hazard in the platform area.

It is understood that this concurrence and the conditions thereof will be attached to and made a part thereof of any instructions issued by the United States Geological Survey to the Union Oil Company, with regard to the use of chemical dispersants pursuant to the present oil seepage in the Santa Barbara channel related to Outer Continental Shelf platform A.

This concurrence is subject to modification or withdrawal upon 24 hours written notice to the U. S. Geological Survey.

Phase II–Cleanup

The involvement of the beaches with oil presented a new set of problems. Absorption of the oil by some means to prevent penetration into the sand was considered to be the first priority. Again the straw mulchers were successfully used both from boats and directly on the beaches to broadcast straw. Removal of the oil soaked straw had to be expedited to prevent its burial by the littoral drift of the sand.

Open beaches and the Santa Barbara Marina received the first concentrated effort. Later, rocky areas and seawalls were cleaned. Limited accessibility in some areas slowed the restoration. The tremendous quantity of driftwood and debris deposited on the beaches and coastline added to the cleanup burden. Severe winter storms had loaded the beaches with trash. Santa Barbara was declared a disaster area by Governor Reagan not because of oil, but because of severe storm damage. Many sewerage treatment plants were damaged or destroyed, filling the nearshore ocean waters at Oxnard, Ventura, Lompoc, Pismo and Santa Maria with millions of gallons of raw sewage. It is estimated that over 30,000 tons of storm debris were cleaned up by the Union Oil Company at no cost to the public agencies.

Supplementary manpower was obtained from the California Department of Conservation. With shutoff of the oil source on February 7, beach cleanup was escalated. The labor force peaked at nearly 1,000 men and supervisors. (An organizational chart is shown in Table 2.)

The beach restoration was principally done with hand labor, raking up straw. In accessible areas on non-rocky beaches, graders, bulldozers and skip loaders augmented the hand labor. Under these circumstances, 50 men aided by four skip loaders, two bulldozers and ten trucks could clean one mile of beach, per eight-hour day.

Rocky beach, sea wall and breakwater cleaning with manual labor, hydroblasters, sandblasters and hot water was slow, arduous work.

One contractor, Bennett International Service, Inc., used a slurry of talc and napththa to dissolve the tarry oil which had dried out on the rocks. The napththa evaporated, leaving a hard crust of oil and talc. The crust was removed by water blasting at 4,000 psig., disintegrating it into a harmless brown dust.

A systems unit, comprising slurry mixing and spraying, a water blaster staffed with nine men, seven of whom were lancemen, averaged about 1,500 square feet per eight-hour day.

Full use of the beaches except for an occasional temporary recontamination was available by June 1, 1969. Seawalls and rocky areas were not finished until August 15.

On February 25, ocean floor seeps had become active to the extent that containment, retrieval and dispersal action was again necessary.

The results of controlled tests indicated that mechanical agitation was as effective as some chemicals in dispersing the type of oil encountered at Santa Barbara.

Even the most effective dispersant (Ara Chem, Inc.) needed effective agitation.

Therefore, two chemical spray boats augmented by as many as 10 power boats for mixing, succeeded in effectively dispersing the seep oil.

A mobile oil skimmer was built, using an original Union Oil Company Engineering Department design for oil retrieval, and put in service.

A unique system of containment was developed by Union Oil Company Oil and Gas Division personnel with cooperation from a fabrics supplier (Firestone Tire and Rubber Co., Coated Fabrics Division). Underwater hoods or tents were installed on the ocean floor to collect the seep oil and carry it through flexible connecting hoses to tanks on the platform. The devices cover some 40,000 square feet of ocean floor and are doing an effective containment job. The first two tents constructed were flat surfaces. Later ones which are 100 x 100 feet are shaped with a predetermined rise in the center giving a pyramidal shape. The tent center is held aloft off the ocean bottom with buoys allowing the gas and oil to migrate toward the tent apex to which the production hose is attached. The gas and oil reach the surface with sufficient pressure to lift the liquid to a tank on the lower level of the platform. The tents are securely lashed to a frame slightly larger than the tents' base dimension. The frame is constructed of 20-inch pipe, reinforced at the corners and equipped with sea-cock and air release valves in each leg. The entire structure is buoyant when the pipe frame is not flooded. If properly lashed, the tent and frame may be slowly towed.

Summary

There was a degree of success in all procedures used in the pollution control efforts.

The use of Corexit met with some success the first day or two of its use. Thin stringers of oil broke up those first days; no oil reached the beaches. However, as the character of the oil changed, neither Corexit 7664 nor Polycomplex A-11 was effective. Arachem Goldcrew dispersant properly applied and mixed, performed well on unweathered oil. Weathered oil could not be dispersed chemically or mechanically.

A qualitative test of the ability of Corexit 7664 and Polycomplex A-11 to disperse crude oil floating on sea water was made on February 9, 1969 near Platform A. Using sea water as the diluent, the dispersants were sprayed on a crude oil slick. The following observations were reported:

1. There appears to be no significant difference in the dispersion ability of Corexit and Polycomplex when Polycomplex is applied at approximately one-half the dosage rate of Corexit.
2. When either Corexit or Polycomplex was sprayed on a black crude slick and not mixed by the wake of a moving boat, very little dispersion of the floating crude occurred at the point of spray entry into the floating crude. There appeared to be a sharp reduction in surface tension. The floating crude oil pulled away from the point leaving a brownish wrinkled floating layer of thicker crude surrounding green water. Microscopic inspection of the brownish layer revealed water in oil emulsion.
3. When either Corexit or Polycomplex was sprayed on a black crude slick and mixed by the wake of the boat moving at 10 knots/hour, there appeared to be good dispersion along the boat's path for a width of 150 ft. Green water was evident in the wake with small patches of black crude spreading out into iridescent and gray films. The boat path remained opened in the slick. After one hour, a bucket sample of sea water from the opened path contained many 0.010" diameter and smaller spherical particles of black oil. Some of the larger particles of black oil floated to the surface in the bucket and broke into an iridescent film. Many of the smaller particles failed to rise to the surface of the sample after one hour of settling.
4. When the boat was run through the slick at 10 knots/hour with no application of dispersants, the slick was dispersed along the boat's path very similar to the runs with dispersants. The boat path remained open in the slick. The bucket sample of sea water from the open path appeared similar to those obtained in the dispersant runs. There were possibly a few more larger spheres of oil that settled to the surface and decayed into an iridescent film.
5. It was concluded that the dispersants tested were not significantly better than the mechanical mixing energy supplied by a boat's propellers when attempting to break up an oil slick in open sea.

The tests were conducted, utilizing the supply ship *Pike I* which is a flat bottom vessel of 130 ft. length, 30 ft. beam and twin screw with 1,300 h.p. All running tests were conducted at 10 knots/hour at an estimated 70% power setting.

The dispersants were applied by pumping 200 barrels/hour of sea water through a 1-1/2 inch pipe by 20 foot long nozzle spray boom mounted forward and two 1-1/2 inch fire nozzles mounted aft. The spray system gave a net 30 foot wide spray application on either side of the vessel. The dispersants were added into the suction of the sea water pump at the following rates (55 gal. bbl.):

Corexit 7664 @ 2-1/2 barrels/hour
Polycomplex A-11 @ 1 barrels/hour

A black crude oil slick of approximately 200 feet width and two mile plus length was utilized for the tests. Thickness of the oil in the slick was estimated to be approximately 1/16 inch thick at the center. The boat cut across the width of the slick during the test runs. Winds were slight at less than three knots/hour from 310 degree compass bearing. Ocean swells were slight (one foot) with no wind ripples.

An evaluation of the oil dispersal properties of Ara Chem Goldcrew dispersant was made on March 2, 1969 The investigator reported:

The system employed for applying the dispersant consisted of a sump pump taking sea water suction, and a second pump taking suction on barrels of the chemical, admixing it with the sea water and discharging the mix through two fire hoses equipped with 90 gpm nozzles at a pressure of 85 psi. The hoses were affixed on each side of the vessel just forward of mid-ship. Application was made by directing the nozzles straight down from the hull then whipping the nozzles, adjusted for a nearly straight stream of water, through an arc of 10 to 15 degres perpendicular to the side of the hull. This resulted in a violent agitation of the water surface for a distance of about six to ten feet. The strength of the stream alone was sufficient to break up the continuity of the oil slick.

Additional agitation of the oil-chemical mix was provided by work boats plying at fairly high speeds across and through the sudsy wake left by the chemical. The suds resulting from application of the chemical are in themselves of little value. Little, if any, chemical action was noted in the foam line. For inner harbor work, esthetics would be better served if no suds were produced.

The chemical as it works, first turns the oil to a dark brownish color. This effect was particularly notable as the work boats plowed through the dispersant boat's wake. The black oil from their bow could be seen turning brown as the chemical-oil mix became agitated together. It is apparent that dispersion, regardless of chemical concentration, is slow and inadequate, unless proper agitation is provided. The volume of oil on the surface at the time the test was made and the combined boat and wave action made it essentially impossible to retrace the boat's course and determine if a clear swath had been established. Even so, the product was doing a good job of dispersing the oil.

Some rather crude hand tests were made using one quart Mason jars to further determine the chemical's effectiveness. By sampling the oil and the chemical mixture being applied, hand mixes were prepared and agitated by shaking. At concentrations of approximately four gallons of chemical per barrel of oil, it was noted that shaking did disperse the oil and that no oil clung to the sides of the jar. Upon standing, the oil re-agglomerated at the surface, but had lost its stickiness. Slight agitation, similar to wave action, would again disperse the oil throughout the jar. Results at such low concentrations would be slow, but with continued wave action would probably be effective.

Where lesser amounts of chemical were tried, some dispersion took place, but the oil came back together on standing and would not again disperse on shaking. A rather rapid conclusion was that a concentration in the area of ten gallons of chemical per barrel of oil would be the most economical and yet effective application of the Ara Chem Goldcrew dispersant.

Later tests on heavily weathered oil proved completely ineffective. Chemical was applied essentially full strength with the result that some iridescent film was released, which could only result in the oil becoming even more sticky and tarry.

No general conclusions should be drawn from the foregoing tests. The results obtained on other crudes under other circumstances could be entirely different. These results are presented only to show the methods used and complexities associated with controlling massive oil spills. Even the passage of time is important for the character of the oil changes and hence the method of control must also change.

A problem in both dispersing and skimming is locating the oil slicks. High-flying spotter planes can guide the boats by radio but detection of the slicks at deck or pilot house level is most difficult.

Both Polycomplex A-11 and Corexit 7664 were used in the Santa Barbara Harbor the night of February 4. Polycomplex A-11 was used to mitigate the fire hazard inside the harbor. Oil had poured through a breach in a section of an inflated boom which deflated when a Santa Barbara Harbor Department boat rammed it. Corexit was used outside the boom at the breakwater entrance and in the vicinity of Stearns wharf and the Underseas Garden aquarium. It is instructive in this respect that although about 1,000 gallons of Polycomplex A-11 and probably an equal volume of Corexit were used to eliminate the fire hazard, no adverse effect on the fish life in the Underseas aquarium was reported.

Booms used for harbor and marina protection were effective except in Santa Barbara. Double booming was used in most instances with straw used to absorb carry-through oil instrusion between the booms. A 500-foot section of the original inflated plastic boom was modified to include filling with plastic foam and with chain weighted skirts, performed well at the entrance to the Channel Islands Marina. No satisfactory offshore boom was found.

A "bubble barrier" installed at the Santa Barbara Marina did not come up to expectations, probably due to inadequate design.

Anchoring of booms offshore was never adequately demonstrated. It appears some sort of mobile thruster system is needed to properly position booms to meet varying current, wind and tide conditions if oil slicks are to be contained in the open sea.

Floating oil skimmers built during the emergency, work well in waves up to six feet and relatively heavy oil concentrations. Although a high percentage of water was pumped, gravity separation readily occurred in the receiving tanks. The oil finally discharged at onshore facilities was a 50% oil-water emulsion.

A catamaran, equipped with a rotating polyurethane drum and wringers (Welles Product Co.), did not find conditions suitable to its operation at Santa Barbara.

Industrial foam sheets were tested and found inadequate for oil pickup.

On Saturday, February 22, 1969, a series of tests were conducted to determine the feasibility of using Scott Industrial Foam to remove or control free oil contamination from the surface of the ocean.

The first tests were run to determine how much oil would be absorbed by foam as it floated freely on the surface of the ocean. The foam used for these tests was 24"x36"x4" samples of Scott Industrial Foam 10 PPI, 20 PPI, 30 PPI, and 60 PPI.

The various foams were put over the side of the boat and directly into an oil slick. They were allowed to remain in the oil for periods ranging from 5 to 30 minutes. The foam was then removed from the oil and examined to check oil absorption and penetration. The penetration was determined by cutting into the center of the 4 inch slabs of foam and observing same. Penetration was approximately 1/2 inch to 3/4 inch in all cases. The surface absorption was visually examined. After each test, an attempt was made to squeeze out the oil that had been absorbed by the foam.

Upon examination of this first test, it was decided that the 20 PPI foam worked best; however, it did not absorb enough oil to make its use for large oil spillage applications practical.

The second test was run on a 24"x36"x4" piece of 10 PPI foam. Weights were attached along one of the 36 inch dimension of the material. The foam was then suspended over the side of the boat from a long pole and emersed in the water so that approximately 12 inches protruded above the water. Lines were attached to the foam so that it could be held in an upright position while suspended at a right angle to the side of the boat.

The boat then proceeded at a slow speed, (approximately two or three knots) through the oil slick. As the foam was moved through the water, it was observed that the water was passing freely through the foam, while the oil remained on the upstream surface of the foam. The foam was then removed and examined. A large quantity of oil was found on the downstream side of the foam. This test indicated that the 10 PPI foam could be efficiently used in the control, or pickup of oil from the surface of water.

The foam could be used to prevent oil from moving from one place to another, or to move the oil from one place to another, or to actually pick up small quantities of oil from the surface of the water.

It is believed the absorption tests were not practical. However, the boom type tests employing the 10 PPI were quite successful and might be developed.

On the beaches, natural clays and talc did not materially aid in oil removal. Straw was effective, but when deposited by the waves and tides in rocky crevices, was difficult to remove. Burning was tried for both oil and straw removal with no success.

The straw mulchers were excellent for a high rate of straw broadcasting both at sea and on the shore. No mechanical straw retrieval system was available or developed. Kelp cutters were considered but none was available. A purse seiner was reserved, but released, when no personnel liability insurance could be obtained.

Rocks, seawalls and the Santa Barbara breakwater were cleaned using warm water, steam, hydroblasting or sandblasting. As previously stated, a naphtha-talc slurry aided the cleaning process in one system.

Some experimenting was done with sinking agents without substantial success. On January 30, 3,000 pounds of equilibrium fluid catalytic cracking catalyst was spread by airplane on an isolated oil slick. The application was good but the slick and catalyst continued to float. Cement, bentonite, talc and diatomaceous earth were also tried at various times with little success.

TABLE 1–DISPERSANT BIOASSAY[1] RESULTS

Dispersant	24-Hour TL$_m$, ppm	96-Hour TL$_m$, ppm
Arachem Goldcrew	128	128
Corexit 7664	15900	7200
Crain OD-2*	125	118
Polycomplex A-11	225	134
Surfemul No.5+	350	350
Unico†	220	220

1. Standard Methods for the Examination of Water and Wastewater, Twelfth Edition (1965).

*Crain Industrial Products Co.
+3C Chemical Corp.
†Universal Supply Co.

A satisfactory method for application of finally divided substances was developed. An oil slick was sprayed with treated United Sierra talc, using a regular foamite fire fighting generator and a boat's salt water fire system. A 1-1/2 inch orifice nozzle and a system pressure of 50 psig were used. Talc could be sprayed fairly evenly on a spread of about 10 to 12 feet. An area of about 1,000 sq. feet was covered in 25 minutes with 500 pounds of talc.

From a nucleus of three supervisors on January 30, 1969, the organization expanded to 36 foremen and supervisors directing the operations (Table 2). By February 11, 1,000 men had been recruited, 18,900 feet of booms were in place, 125 pieces of mechanical equipment, 54 boats of all types and 3,000 tons of straw were on hand or had been dispersed. (Appendix I). Security guards and traffic directors had been stationed. Daily planning and reporting was in effect. (Appendixes II & III). A radio transmitter-receiver had been installed in the headquarters office. Walkie-talkies were in use in the field. These radios were very valuable. Much time was lost in the first week due to lack of communications.

The disposal of mountains of storm debris along with oil-soaked straw and sand was a very serious problem. A tremendous quantity of wood, trash, leaves and kelp, deposited on the beaches and shores by severe winter storms, was oil-covered and had to be removed. Legal disposal sites were limited. Santa Barbara city officials did not permit the use of the city dump. The Santa Barbara county dump was inaccessible because of a road wash-out. Ventura and Oxnard sites were quickly overtaxed. Many loads were hauled to Fillmore, over 50 miles distant. The

TABLE 2– ORGANIZATIONAL CHART
Company Coordinator – Operations Manager

Sandyland Area	Beaches Harbors	Ventura Area	Planning	Boats, Sea Operations	Communications	Wildlife	Supplies Equip.	Nights
					Supervisors			
(1)	(20)	(3)	(1)	(1)	(3)	(1)	(2)	(2)

City and County of Ventura and the City of Carpinteria authorized burning on their beaches at certain locations which materially aided the cleanup there. (Appendix IV).

The insurance carriers arranged for the cleaning of some 1,000 boats and provided crews to clean private seaside homes and yards, which had been fouled by oil during high tides and storms.

There was at no time any shirking of responsibility by the Union Oil Company or its partners, Gulf, Mobil or Texaco, in restoration of the Santa Barbara-Ventura coastline to its original beauty and charm. The present cleanliness of the area stands as testimony of the ability and willingness of the members of the petroleum industry to fulfill both their legal and moral obligations at all times and under all conditions.

APPENDIX I–EQUIPMENT LIST

Boats

Name	Owner	For Use As
1. Coast Tide 76'	Tidewater Marine	Straw spreader
2. Sea Truck 65'	General Marine Transport	Straw spreader
3. Zelma 54'	General Marine Transport	Boom tending
4. Pike I 135'	WODECO	Spraying and Skimming
5. Pike II 30'	WODECO	Boom tending
6. Oil City 100'	Port Hueneme Ind. Serv.	Spraying
7. Trojan 100'	Pacific Towing	Spraying
8. Petrel		Tug
9. RS-23 135 x 45'	Crosby & Overton	Boom tending–Ventura
10. Mary K	Private fishing boat	
11. Mary K Skiff	Private fishing boat	
12. Genes Folly	Private fishing boat	
13. Pieface	Private fishing boat	
14. Bonanza	Private fishing boat	
15. Sea Mistress	Private fishing boat	
16. Six Pak	Private fishing boat	
17. Gaviota	Private fishing boat	
18. Skiffs (2)	Rental	

Booms

1. 6" Foam float with 6" skirt @ 1800' – Hutchison
2. 28" Inflated sea curtain – 30" curtain @ 1000' – Union Oil Co.
3. Log boom @ 2000' – Union Oil Co.
4. Union Oil Co. 1000' plastic boom from Marine Terminal
5. Union Oil Co. 4 x 4 wood boom – 200'
6. Crosby & Overton – 3100'
7. U.S. Navy – 900'
8. Log boom 2000' – due 2/5/69
9. Plastic boom – 500' – due 2/5/69

Heavy Cleaning Specialists

1. Crosby & Overton

Chemical Services

1. Enjay Chemical Co.

Chemicals

1. Corexit 7664	120 drums	Santa Barbara
	99 drums	Stanton
	80 drums	Stanton (due 2/5/69)
	72 drums	Oakland
	800 drums	Houston, Texas
	650 drums	Bayonne, N. J.
	400 drums	Misc. U.S. cities
	10 drums	Santa Barbara
2. Polycomplex A-11		

Aircraft

1. Durden Bros. – Fish spotting service (for positioning boats)
2. Rotor Aids – Observation and transportation

Miscellaneous Equipment

1. Baker tanks (2) mounted on barge RS-23
2. Haliburton pumps (2) 1 on Pike I–skimming; 1 on RS-23–skimming
3. Crawler Crane (5) Ton mounted on RS-23
4. Essick pump 6"
5. Welding machine (rental)
6. Pick-up truck (6) (rental)
7. Food stores for U. S. Navy YO-223
8. 5000 lb. anchor–General Marine Transport
9. 1000 lb. anchor (2)–General Marine Transport
10. 250 lb. Danforth anchors (2)–Ocean Science and Eng.
11. 200 lb. Danforth anchors (3)–Ocean Science and Eng.
12. 150 lb. Danforth anchors (3)–Ocean Science and Eng.
13. 60 lb. Danforth anchors (6)–Ocean Science and Eng.
14. Round buoys 35" (3)–Ocean Science and Eng.
15. Round buoys 72" (3)–General Marine Transport
16. Can buoys 24" dia.x 30" (6)–Ocean Science and Eng.
17. Polyform buoys 30" dia. (4))–Ocean Science and Eng.
18. Polyform buoys 18" dia. (2)–Ocean Science and Eng.
19. Polyform buoys plugs (6)–Ocean Science and Eng.
20. Galv. chain 1/2" (343')
21. Wire rope–misc. sizes–10,000'
22. Shackles–misc sizes–(100 est.)
23. Cable clamps–misc. sizes (2,000 est.)
24. Shovels (200)
25. Rakes (180)
26. Nylon line 1-1/4" (400')
27. Manilla line–misc.
28. Snow shovels (100)
29. Pitch forks (150)
30. Fibre drums (1000)
31. Buckets, 5 gal. (100)
32. Fertilizer spreaders (for talc)
33. Hand cleaner (100 gal.)
34. Push brooms (100)
35. Straw (100 tons/day)
36. Mulch spreaders (3)–boat mounted
37. Flat bed truck, 3 ton (3)–Crosby & Overton
38. Talc (3 tons)
39. Ekoperl (600 bags)–due 2/5/69

APPENDIX II - PROGRESS REPORT (DATE)

Santa Barbara Area - Beaches and Harbor

Gaviota - Stack and burn at Bulito, burn debris at Augustine. Van Construction - 23 men (2) loaders, (1) grader.

Goleta Park - Stack and burn debris. Hutchison - 11 men.

UCSB - Stack and burn debris, haul to Tajiguas dump. Hutchison - 8 men, (1) loader, (1) grader, (1) dozer, (7) trucks, (42) loads.

Miramar - Clean beach and haul debris. Crosby & Overton - 18 men. (2) loaders, (11) trucks, (49) loads.

Bonnymede - Wash rocks, stack debris. Crosby & Overton - 10 men.

Padaro Lane - Wash rocks, haul debris. Crosby & Overton - 13 men. Haul (6) loads.

Summerland - Stack and burn debris. Crosby & Overton - 6 men.

Rincon Point - Stack and burn debris. Crosby & Overton - 15 men. (2) loaders.

Harbor - Sandblast rocks at Undersea Gardens, hydroblast seawall, clean boat slips and walkways. Hutchison - 15 men. Crosby & Overton - 3 men. (2) hydroblasters, (2) punts, (1) skiff, (1) sandblaster.

Stearns Wharf - Crosby & Overton - 3 men.

Santa Barbara Area - Contractors and Equipment

34 men - Hutchison & Sons
62 men - Crosby & Overton
23 men - Van Construction
5 - guards
18 - dump trucks
97 - loads hauled
3 - graders

6 - loaders
1 - dozer
2 - hydroblast
1 - sandblast
0 - steam cleaner
1 - burner

Supplies and Material

Diesel - 966 gal. Gasoline - 105 gal. Solvent - 55 gal.

Boat and Sea Operations

Winn - Oil skimming
Judy 10 - Work with Winn
Seatender - Drilling operation
Mallard - Drilling crew change
Packer - Construction operation
Swallow - Construction crew change
Mary K. Skiff - Maintain boom in harbor

Chemicals

55 gal. sprayed at Platform A. Total to date from 2/26/69, 426.5 bbls.. 1 bbl. = 55 gal.

Ventura Area - Beaches and Harbor

Channel Islands - No oil in harbor - boom open. 7 men days - 6 men nights.

Port Hueneme - No oil in harbor - boom open. 2 men days - 4 men nights.

Point Mugu - No oil in harbor - boom open. 4 men days - 4 men nights.

Hollywood - Rake, stack and haul debris. Van Construction - 15 men. (3) loaders, (6) dumps.

Silverstrand - Rake, stack and haul debris. Van Construction - 14 men. (1) loader, (4) dumps.

Emma Wood, Hobson, Sea Cliff Arco areas - Steam clean seawall, haul debris. Allied Construction - 20 men, (1) crane, (3) loaders, (6) dumps, (2) steam cleaners.

Burn area - (1) D8 dozer, (1) fuel truck, (1) water truck

Guards - 6 men hay yard, 6 men burn area

APPENDIX III - PROGRESS REPORT (DATE)

Beaches and Harbors

A sand dike was constructed across the upper end of the beach lagoon adjacent to the bird sanctuary on East Beach. After diking, the slough was drained and cleaned. This was done at request of the City Park Department.

At Carpinteria State Beach, 150 inmates were used in cleaning beach and stockpiling. Debris burning continued.

Crosby-Overton forces were employed at oil wells near Summerland cleaning beach and stockpiling. Beach cleaning and stockpiling continued at Serena and Sandyland areas. Crosby-Overton employees were used at these locations.

Sixty inmates were used at the main Santa Barbara beach, raking and stockpiling. This beach has been worked, using Cat driven hayblowers as well as hay blown by Pike I. This beach is again in good shape.

Two different types of commercially available powered hay rakes were tried on this beach with no success.

Equipment used entailed: 6 small trucks, 11 loaders and one low bed truck.

Ventura Area

Ventura harbor remains clear of oil. Plans have been finalized for the following activity on 2/18:

Construction of a mounded buffer along the upper portion of Mandalay Beach.

Seventy-six conservation crewmen on Ventura beach proper to clean and stockpile. Burning will be started on 2/19.

Approximately 20 persons from Allied Construction Co. to clean beaches and steam clean sea walls at Seacliff in the Rincon Beach area.

Channel Islands - boom across harbor has been reset to provide a gate for easier passage of ships. Harbor remains clear of oil.

Port Hueneme - harbor remains clear of oil. Boom is open between 6 a.m. and 7 p.m. and is closed at night.

Point Mugu - remains clear of oil. Little activity in this area.

Planning

Ventura area clean-up was planned. Several hours were spent with THUMS personnel on explaining various types of booms. The beach area from Santa Maria south will be surveyed early on 2/18.

Boats and Sea Operations

Approximately 30 tons of straw were sprayed from the *Pike I* along the southern Ventura area, Santa Barbara Harbor area and about five miles outside of Santa Barbara. Hay was reloaded at Sterns Wharf and on the *Pike I* for continued spraying on 2/18.

Communications

Manager of Undersea Gardens was approached in regard to his water intake. Found that he's pumping from within the inner harbor area instead of from the outer harbor. He has had no problems with water quality. They are very appreciative of Union Oil efforts.

Cleaned all material from Navy pier in compliance with Harbor master's request.

Arranged for steam cleaning of dredge and first walkway of Marina I on 2/18. Have had some complaints of slippery conditions on this particular walkway.

Rigged skiff with clean hose and water pumper to start flushing of oil from individual boat slips in the inner harbor.

Installed mounted radio in truck P-104 and issued truck to Goyette to improve communications from the outlying areas of work. Will install two more radios in P-104 to further improve outlying communications.

Wildlife

Latest count: 4 p.m. - 2/16 - 1,146 treated; 311 recuperating; 141 DOA; 835 died after treatment.

This unit will probably be held at one or two men in case activity should increase. The recuperating birds are being transferred on 2/18 to the Child's Zoo.

Supplies - Equipment

Two deck scrub brushes; eight - 5 yd. loads 1-½" rock; five bundles rags; one case hand cleaner.

Nights

Maintained air curtain and boom surveillance.

An accident occurred during the night when a ship struck the floating air curtain being installed. Extent of damage unknown at this time.

APPENDIX IV - SANTA BARBARA CLEAN-UP OPERATION

Date	Loads Hauled	Dump Trucks
2/10		54
2/11	400	
2/13		6
2/15	23	
2/16		2
2/19		2
2/20		6
2/21	90	13
2/25	19	
2/26	80	20
2/27	138	30
2/28		4
Total Feb.	750	137
3/1		21
3/2	179	24
3/3	104	26
3/4	183	36
3/8	130	29
3/10	94	32
3/11	106	35
3/12	91	36
3/13	53	37
3/14	49	14
3/17	70	32
3/18	86	30
3/19	97	18
3/20	57	19
3/21	43	10
3/24	80	20
3/25	87	22
3/26	84	22
3/27	144	21
3/28	192	22
3/31	153	23
Total Mar.	2082	529
4/1	176	23
4/2	157	23
4/3	35	25
4/4	96	20
4/7	97	21
4/8	86	29
4/9	140	21
4/10	152	22
4/11	166	21
4/14	221	27
4/15	201	25
4/16	147	23
4/17	299	24
4/18	272	21
4/21	59	22
4/22	106	20
4/23	159	24
4/24	241	29
4/25	240	24
4/28	240	28
4/29	384	28
4/30	329	29
Total Apr.	4053	529
5/1	391	57
5/5	132	23
5/6	196	22
5/7	258	25
5/8	220	24
5/9	266	21
5/12	241	24
5/13	157	24
5/14	145	24
5/15	189	25
5/19	208	26
5/20	187	24
5/21	104	24
5/22	55	13
5/23	53	9
5/26	25	10
5/27	31	7
5/28	32	10
5/29	51	7
Total May	2941	399

FATE AND BEHAVIOR OF OIL ON WATER

Wednesday, December 17, 9:00 a.m.

Chairman: Dr. C.M. Tarzwell
Director, National Marine Water Quality Laboratory
Federal Water Pollution Control Administration

Co-Chairman: H.A. Bernard
Chief, Agriculture and Marine Pollution
Federal Water Pollution Control Administration

Identification Of Oil Spills:
Comparison Of Several Methods

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Abstract

Based only on analysis of oil slicks, several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques.

We have examined three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three methods of active tagging (halogenated polycyclic aromatics, organometallics, and coded microspheroids). Passive tags cannot be recommended because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized; even if these processes do not occur, they can create formidable forensic problems for the prosecution and telling counter-arguments for the defense. Since active tags are designed to be stable and identifiable, they are made for the job; we have found promise and merit (though unequal) in the three types of active tags we reviewed.

General

According to the U. S. Coast Guard, there were 714 major spills in U. S. waters in 1968; in 1966 there were 371. These Coast Guard reports do not tell the whole story, for many oil spills are never reported to them. According to various official estimates, the true figure is more probably several thousand than several hundred. The problem of oil pollution is patently serious, and grows more serious with time. One of the great problems in combatting oil pollution is to identify the pollutor: oil pollution is illegal under at least six statutes of the U. S. Code.

While small amounts of oil pollution can come from thousands of sources, a great deal of oil pollution apparently comes from a few types of sources: tankers, offshore wells, storage tanks, and pipelines. Waterborne sources account for over half the pollution. While the problem is large, it is not infinite. There are 14,000 offshore wells, and 2,000 tankers making about 10,000 calls a year on U. S. ports. And only 400 of these fly the U. S. flag. The largest potential sources of pollution are few in number. The problem is: how to legally trace pollution to them, cheaply and unambiguously?

The most direct approach to tracing pollution is to compare the slick with the oil carried by the suspect source. This approach assumes that the slick will not differ significantly from the true source, and this assumption is justified if the word "significantly" is loosely construed. Everyone familiar with oil pollution knows about the weathering of slicks, and few would argue that the "chocolate mousse" variety of oil emulsion is significantly similar to any commercial petroleum product. The real problem is: how much weathering makes a slick unidentifiable? We shall presently return to this question.

Weathering: Chemical and Microbial

Oil is no simple compound or mixture of compounds. Crude and fuel oils show enormous variation in chemical content, both qualitatively and quantitatively. Naturally, variations in chemical makeup are accompanied by variations in physical properties. Perhaps the most important event in the history of an oil slick is the evaporation of the light fractions.

While the rate of evaporation will be influenced by many variables, after several days at sea the slick will consist almost entirely of compounds whose boiling point is above 370°C (approximately 700°F),[1] viz compounds containing at least 20 carbon atoms, and probably of complex chemical structure. When oil is spilled on calm water, it rapidly spreads to a film about 2 cm thick. Although many variables affect its subsequent thinning, its final thickness will be 10-100 microns on pure water, but approximately 1mm on heavily contaminated water.[2] Thin films offer a larger surface (and hence, are more easily acted upon by the environment) than thick films.

While evaporation undoubtedly accounts for most of the volumetric loss in the slick, solution in sea water may also play a significant role. R. A. Dean[1] has argued that, while the lightest hydrocarbons have finite solubilities in water, some heavier petroleum constituents, while undoubtedly less soluble, may still go into solution, for we are considering huge volumes of sea water. Dean has contended that if we assume a solubility on the order of one part per million, the whole cargo of the *Torrey Canyon* could have been dissolved in a patch of sea 20 miles square and 500 feet deep. In this connection, the presence of surfactants in natural crudes (surfactants such as porphyrins and metalloporphyrins) assumes a new significance. Moreover, trace metals in petroleum are often in water-soluble form, or become water-soluble as the slick weathers.

While the slick is spreading, evaporating, and being leached of its water-soluable components, other processes act upon the residue: catalytic autoxidation, photochemical oxidation, polymerization, and microbial oxidation. While we all acknowledge the fact that oil changes its character because of oxidation, solar radiation, and microbial action, we have little information about the specific operant mechanisms, reaction times, and reaction products.

The unsaturated, alkyl-aromatic, and alicyclic hydrocarbons in petroleum are probably oxidized to acids via peroxide, hydroperoxide, alcohol, and ketone intermediates.[3] In spite of the absorption of the shorter wavelengths of the sun's rays by the atmosphere—which reduces the ultraviolet light (UV) of less than 4000 Å to no more than 5 per cent of the total—there remains enough energy in the residual radiation to break a variety of chemical bonds;[4] in general, aromatic hydrocarbons are more stable than aliphatic hydrocarbons to UV and visible radiation. Ellis & Wells[5] have reported that solar UV causes oils to become colored and gummy in the presence of oxygen, and that the rate of gum formation triples for every 20°F rise in temperature. Wolsky & Chapman[6] have shown that UV caused porphyrins to disintegrate rapidly in the presence of oxygen. Oil slicks are also attacked by oxidizing microflora, which are common in both fresh and salt water.[7]

While many of the compounds in petroleum are undoubtedly metabolized, the metabolic pathways for large and complex hydrocarbons are not well established,[8] and the kinetics of oxidation (even for the smaller hydrocarbons) seem to be rather slow. It is well to bear in mind, however, that the species distribution of saprophytic microorganisms varies widely with latitude, and that diversified enzymatic activity is much more common in cold-water than in warm-water bacteria.[9] The question of microbial oxidation and assimilation of petroleum compounds is further complicated by the anomalous phenomena of co-oxidation and oxidation of nonassimilable substrates, which have been reviewed by McKenna & Kallio.[10]

Passive Tagging

We have already raised the question of how much weathering makes an oil slick unidentifiable, but cannot answer it apart from a critical analysis of methods of identification. There are two general approaches to identification, which are sometimes called active tagging and passive tagging. Passive tagging is a convenient circumlocution for no tagging at all: nothing is added to the oil; the slick itself must provide all the evidence for its own identification.

Active tagging involves adding some known and readily identifiable material to the oil. The added material must satisfy several criteria: it must be soluble or dispersible in oil and insoluable and nondispersible in water; it must be easily detectable in extreme dilution; it must be chemically and physically stable in both spilled and unspilled oil; and it must not interfere with the commercial uses of petroleum. One additional criterion: it must not be too expensive. Two figures of speech are helpful in distinguishing active tagging from passive tagging: Passive tagging amounts to a "fingerprint," and active tagging amounts to a chemical or physical "license plate."

Heavy Hydrocarbons

Let us consider passive tagging first. We have seen that when oil is spilled, it may be irradiated; mixed with complicated aqueous solutions (sea water, polluted fresh water, or brackish swamp water); exposed to oxygen and air pollutants; and intimately associated with a variety of aquatic microbes; depending on local conditions, it may have been partially evaporated, emulsified, photolyzed, autoxidized, polymerized, enzymatically oxidized, and may have undergone ionic exchange.

What part of the fingerprint can be stable to all these conditions? Heavy and highly branched alkanes are excellent candidates; so are the heavy and complex hydrocarbons of mixed structure that are common in lubricating oil. However, the heavy branched alkanes are generally exceedingly rare in oil, because the concentration of branched-chain paraffins in crude oil is a rapidly decelerating function of molecular weight.[11] The mixed-structure hydrocarbons common in lubricating oils permit an almost infinite number of structures, and the likelihood of positively identifying any one of them becomes vanishingly small.[12] After all, even though several hundred compounds have been identified in crude oil, the identified compounds "probably account for well under 50 per cent of the constituents of a crude petroleum."[12] It should be apparent that the hydrocarbons in slicks of crude and heavy oils will contain an even higher percentage of unidentified structures. One must therefore conclude that although heavy, complex hydrocarbons are likely to be stable constituents of oil slicks, they will not serve as passive tags because they are exceedingly rare, exceedingly difficult to identify, or both.

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[1] Superior numbers refer to literature references at conclusion of text.

Trace Metals

What other constituents of oil might be used as a fingerprint? Trace metals (especially vanadium and nickel) and isotopic ratios have been suggested, and these will be critically reviewed next.

Many inorganics have been reported in petroleum ash; we had no difficulty finding reports of 37 inorganics, and the list could no doubt be extended. Many of these elements are rarely found, others are rarely found in high concentrations; only a few are frequently found in petroleum ash in concentrations above 0.1%, and of these few, special importance attaches to vanadium and nickel.

These two metals are important because of the problems they cause industry. Like most elements of the first transition series, both are dehydrogenation catalysts (nickel is about 10 times more potent that vanadium), and both are commonly found in petroleum as volatile compounds. For this reason, they are often found in distillate fractions, their concentration increasing with the depth of the cut. Some of these volatile organometallic compounds alter the selectivity of cracking catalysts, increasing the formation of coke and hydrogen and decreasing the yield of gasoline. Non-volatile vanadium, which concentrates in the residuum from which heavy fuel oil is produced, is extremely corrosive to fire-clay bricks used in furnaces; the vanadium oxides form low-melting eutectics with clay, producing hard, glassy slags that are extremely difficult to remove.[13,14]

Both vanadium and nickel are commonly found in petroleum as compounds of widely varying molecular weight.[15] Often, these compounds are water-soluble inorganics.[16] Of the organic compounds, special importance attaches to the nickel and vanadyl metalloporphyrins because these compounds are rather stable constituents of petroleum and have great geochemical significance.[17] It is well to remember, however, that only a small fraction of nickel and vanadium in petroleum is usually found in porphyrins.

While vanadyl and nickel porphyrins are rather stable compounds, they are also interfacially active and tend to concentrate at hydrocarbon-water interfaces. In light of this property, several workers have used water sprays to extract metalloporphyrins from oil; this method is thoroughly established.[16] Wolsky & Chapman[6] have also shown that when porphyrins are irradiated by UV in the presence of oxygen, they are rapidly decomposed. Furthermore, while the metalloporphyrins in oil usually have reduced side chains, oxidizing conditions usually result in polycarboxylic porphyrin structures, which have a very marked affinity for water interfaces.[18] Indeed, Falk[19] has demonstrated an almost linear relationship between the number of carboxyl groups on a porphyrin and the porphyrin's mobility in a solvent system of lutidine and water.

In view of the fact that both the vanadium and the nickel in petroleum are often volatile and water-soluable, it is difficult to understand why they have been seriously recommended as passive tags. Nevertheless, they have been recommended off and on since 1955, if not before. Since all the recommended methods require sampling of oil slicks–which will have been partially evaporated, thereby concentrating the involatiles–it is pointless to compare the absolute metallic contents of the slick with that of the unspilled oil. Rather, the ratio of metals (in particular, the ratio of vanadium to nickel) must be assumed constant. This strikes us as a perilous assumption, since (in general) nickel compounds in petroleum are usually reported to be more volatile and more water-soluable than vanadium compounds. The arguments advanced for vanadium and nickel tags are quite often mistaken on matters of fact:

> Vanadium and nickel are held in the oils as coordinated complexes with porphyrins, and are not affected by contact with sea water. . .[20]

or from a more recent proposal:

> The method simply entails measuring the vanadium and nickel contents of the unknown oil pollutant. There is a very specific amount of these metals associated with every crude–in essence constituting an individual metallic trait. There are other chemical and physical properties for the various crudes, but these are subject to change during weathering/aging [sic]. The metallic components, however, are stable and are not affected by weathering. By simply comparing the metallic content of the spill against [sic] that of the suspected source, it is possible to limit the probable source to a specific vessel, pipeline or storage facility.[21]

Others have proposed analyzing even larger metallic suites, for example, vanadium, sodium, manganese, and cobalt; this method was proclaimed to offer

> definite promise for the trace-element characterization matching [sic] of an actual oil-slick sample with one sample of fuel oil–out of a number of suspect samples. . . . The various characterizing trace elements, occurring in the original crude oils largely as essentially non-volatile metal porphyrins, remain in the residue left when the volatile components of the crude evaporate (as from an oil slick), and when the light ends are distilled of in refining. Thus NAA [neutron activation analysis] matching of the levels of these trace elements–between an oil slick and its polluting source–may, for the first time, provide a method of identification of the source of oil pollution of waters that will aid in the enforcement of present oil pollution laws.[22]

While the idea of using vanadium and nickel to identify oil slicks has, at the very least, the merit of being based on some firm fact–for vanadium and nickel are very commonly found in oils, and they are often found (in small part) as metalloporphyrins, of which they are by far the two most stable[18]–these other metals, especially sodium, are very poorly advised. Sodium, for example, is common in petroleum but it is also the most common cationic metal in sea water;[23] it is therefore readily available to participate in exchange and replacement reactions with the oil slick. The petroporphyrin nucleus is an obvious target for exchange reactions with sodium ions from the sea; unfortunately, these sodium porphyrins are not very stable in the presence of other cations.

Hodgson[18] and his colleagues have brilliantly summarized the evidence: It is thoroughly established that alkali metal ions in porphyrin molecules are readily replaced by other cations; the metalloporphyrins, in order of increasing stability, is alkali metal, large divalent metal, and finally small divalent metal; and complexes of porphyrins incorporating monovalent cations show rapid exchange.

It has been known since the late 1940's that both the mono- and di-salts of porphyrins with alkali metals are very unstable and break down in the presence of water. While other petroleum compounds of sodium may be more stable than sodium porphyrin, it is well to remember that one general characteristic of sodium compounds is their water solubility, and water-soluble compounds are not likely to remain in an oil slick for long.

The Relevance of Market Statistics

Quite aside from the physical and chemical stability of metals in petroleum, there is the problem of distinguishing two or more samples that may be very similar. While the vanadium/nickel ratio of Kuwait petroleum is quite different from the corresponding ratio in Venezuelan petroleum, the U. S. does not import equal amounts of petroleum or petroleum products from these two countries. For example, about 80 per cent of the residual fuel oil imported into the U. S. comes from Venezuela and the Netherlands Antilles, and over 90 per cent of all the residual fuel oil that is imported by the U. S. is received in PAD District 1 (roughly, the New England, Middle Atlantic, and Southeastern States).[24]

Imported residual fuel oil is far more likely to be spilled in an East Coast harbor than in a Pacific harbor, and the oil is very probably a South American export. Similar considerations apply to other petroleum products. Sumatran crude oil, for example, is imported almost exclusively into the Pacific region; Venezuela and Canada together account for about two-thirds of the crude oil imported into the U. S. Exactly the same argument also applies to oil produced within the U. S. Texas, Louisiana, California and Oklahoma together produce about 80 per cent of our crude oil. Much of this oil comes from such giant fields as Wilmington, East Texas, and Kelly-Snyder. It is therefore likely that a spill of U. S. crude oil is a spill of oil from Texas, Louisiana, California, or Oklahoma, and it is quite likely that this oil came from one of the major oil fields in those states.

The more specific the argument gets, the greater the likelihood becomes. For example, most of the crude oil that is processed by the great refineries of Eastern Pennsylvania and New Jersey is sent via tankers and barges from Texas and Louisiana; it therefore follows that a spill of crude oil on the Delaware River almost certainly involves Texas or Louisiana crude, and very probably involves a crude oil from one of the large oil fields in those states. How can vanadium/nickel ratios be used to distinguish one Wilmington crude from another, or one Venezuelan residual fuel oil from another? The economic realities are not especially relevant to a pure chemical argument, but in a discussion of the probability of oil spills, they should not be entirely forgotten either.

Sulfur-Isotope Ratios

Keeping this discussion of economic realities in the back of our minds, we can proceed to the use of sulfur isotopes as passive tags. This discussion is heavily based on the work of Thode and his colleagues[25-28] at McMaster University (in Hamilton, Ontario), who have been studying sulfur-isotope ratios in a variety of geologically important materials, including petroleum, since the later 1940's. As in our discussion of metallic suites in petroleum, we have chosen the work of disinterested scientists whose work was conceived and published without oil tagging in mind; Thode and his colleagues have undertaken a purely geochemical investigation of isotope fractionation.

Isotope fractionation is an established and important geochemical process: Oceanic carbonate is rich in 0-18 with respect to ocean water, plants are enriched in C-12 with respect to atmospheric carbon dioxide, and sea sulfate is rich in S-34 with respect to the sulfur found in meteorites and basic igneous rocks.

Although there are nine sulfur isotopes, only four of them (S-32, -33, -34 and -36) occur in natural sulfur; all four are stable, but they are not equally distributed: S-32 predominates (95.0 per cent), and S-34 (4.22 per cent) accounts for most of the remainder. The ratio of these two most common isotopes is often standardized with respect to meteorites because this ratio is virtually invariant; in the Earth's mantle, however, the content of S-34 varies by approximately 100 per cent. The 34/32 ratio has been studied in many materials, including petroleum and sea water: In sea water the ratio is +20 ±2 per cent, while in petroleum it varies from -8 per cent to +33 per cent—indeed, it varies from -8 per cent to +28 per cent in petroleums from Utah alone! And the apparent significance of this phenomenon has not been lost on proponents of passive tagging.

The fundamental fact in the geochemistry of sulfur isotopes is that S-34 tends to sulfate and S-32 tends to sulfide: S-32 is the more readily reduced isotope and S-34 is the more readily oxidized. 34-Sulfide plus 32-sulfate tends to 32-sulfide plus 34-sulfate. In short, the heavier isotope is more readily oxidized, and the lighter isotope is more readily reduced.

While all the sulfur compounds in petroleum have not yet been identified, all the identified sulfur compounds are reduced: thiols (mercaptans), disulfides, sulfides, and thiophenes.[15] The ultimate source of this sulfur is not definitely established, but many authorities have argued that it must usually be oceanic sulfate, reduced to sulfide by such bacteria as *Desulfovibrio desulfuricans;* Davis[7] has beautifully summarized the evidence. These bacteria preferentially metabolize the lighter mass isotope, viz, S-32, and it has been shown by several investigators that this preference is usually around 15 per cent;[29] the 34/32 ratio in petroleum should therefore be about 15 per cent lower in petroleum than in the sulfates of ancient oceans.

The group at McMaster University has shown that this is usually the case. This group has shown that, while the absolute sulfur content of petroleum declines with time, the sulfur-isotope ratio stays remarkably constant. They have also shown that the content of sulfur isotopes in Devonian petroleums extending from the 49th Parallel to the Arctic is nearly constant, and have argued that the most reasonable explanation for this phenomenon is a large sea, which provided the large reservoir of sulfur of uniform isotopic content and constant oil-forming conditions. They were therefore pleased to announce that the isotope ratios in Ordovician and Silurian oil of Texas and Ontario, although separated by several thousand miles, were quite similar.

What is the conclusion to be drawn from this evidence? It is, quite simply, that S-isotope ratios are just another general index of geological age. Geochemists have several such indices (e.g., ratio of complex cyclic structures to simple chain structures, not to mention radiocarbon dating). It is difficult to see, however, how any such index can be of much use in identifying oil spills. For example, our largest foreign source of oil (Venezuela) is a major shipper of Tertiary crude; so is Louisiana, our second most productive oil state.

Our second largest foreign source of oil (Canada) sends large quantities of pre-Mississippian crude to our East Coast refineries; so does Texas, our largest oil-producing state. Miocene oil is common in Louisiana; it is also common in Indonesia. Are S-isotope ratios sufficiently precise to distinguish Miocene from Eocene? If not, oil from Fresno, California, can't be distinguished from the oil of Sanga Sanga, Borneo, or Plaquemines Parish, Louisiana.[24,30]

There is another objective, however, that may be even more important. The sufur in oil is reduced, but when oil is spilled at sea, the sulfur is put in an oxidizing environment. Because of kinetic isotope fractionation, the S-34 will be more readily oxidized that the S-32, other things being equal. The logic of this process leads us to conclude that the more the spill is oxidized, the lower the 34/32 ratio will be; a week-old oil spill should have a lower isotope ratio than a day-old spill from the same source. If the fractionation effect were strong enough, the delta-value might go from highly positive to very negative. This combination of geochemical fact, oxidation kinetics, and petroleum-trade statistics leads us to conclude that sulfur-isotope ratios could not very well be used to prove a violation of oil-pollution laws.

Special Cases

While we do not know of any easily identified passive tag that is unaffected by harsh or extended weathering, several kinds of passive tags can be used profitably as presumptive tests on the identity of oil spills under special conditions. In general, the requirements on passive tags should not be different from the requirements on active tags: Both kinds of tags should be unchanged by weathering and microbial oxidation, soluble or dispersible in oil, insoluble and nondispersible in water, and involatile.

However, there are special circumstances in which some of the requirements on passive tags may be replaced. Where oil pollution is infrequent, where there are few possible sources of pollution, and where weathering may be assumed to be inconsequential or insignificant (because of the slick's freshness), several methods of chemical analysis–supplemented by a great deal of convincing circumstantial evidence of an extra-chemical kind–may identify oil slicks by passive tags in the spilled oil.

Chemical analysis is useful when it does not have to bear the whole burden of proof. For this reason, we cannot agree with authorities who propose a combination of analytical techniques (such as gas-liquid chromatography, controlled pyrolysis, mass spectrometry, and computer calculations) to yield a "fingerprint" of the slick.[31] If the spill has not been extensively weathered and if there are not many possible sources of pollution, the combination of analytical techniques is wasteful: Where the circumstantial evidence is convincing, extensive chemical analysis is not required. However, where there are many possible sources of pollution, where pollution is frequent, and where the spill may have been weathered for days or weeks (or mixed with other spills, some of which may have been weathered), it seems highly improbable that any combination of analytical techniques could stand up in court to a carefully reasoned chemical defense.

The problem of mixed and continuous pollution is not unknown. According to Ludwig and his colleagues,[32,33] the beaches in Southern California are commonly polluted by a mixture of oil and asphalt from natural seepage, liberally supplemented by tanker and drilling wastes. One would expect that similar conditions frequently pertain along the Gulf Coast. A senior scientist at the Woods Hole Oceanographic Institution was recently reported[34] to have said that he could not sail anywhere in the Atlantic–even a thousand miles from land–without finding oil. The methods we shall discuss cannot be recommended for such areas as Southern California, nor for areas that are frequently afflicted with oil pollution.

To begin, all the methods of passive tagging we have already discussed can be used (although they are more expensive than several other methods) as long as there is plenty of independent evidence that the oil slicks are fresh and have not been mixed with other oil pollution. Other simpler methods of identification were published in the U. S. and England in the early 1950's; these methods make use of simple techniques of paper chromatography.

Schuldiner[35] reported (in 1951) a simple method of spot chromatography that had produced evidence for prosecuting and convicting oil polluters in Baltimore, Maryland, and the upper Chesapeake Bay area. He sampled the oil slick, then boarded suspected ships and sampled bunker fuel oils, bilges, loose oil on the decks or sides of the vessel, on fuel intake valves, and on adjacent docks. The samples from the slick and the ship were strictly treated as comparison samples. Small spots of the samples were applied to blotting paper, allowed to develop completely (i.e., to stop spreading), and were then examined under ordinary and UV illumination. He found that various crude, semi-refined, and refined petroleum products gave characteristic spot chromatograms, and that the chromatograms from known crudes invariably gave identical radial fluorescence patterns.

While Schuldiner's chromatograms can be effective, they are not perfect: They entail at least three troublesome problems. First, confluent multiple spills will give chromatograms that are characteristic of the mixture, not of the components of the pollution; it is very doubtful that the chemical mixture can be resolved into its legal components, or that a given slick can be proved not to be a mixture unless the circumstantial evidence is overwhelming. (This objection applies with equal force to all other methods of passive tagging.) Second, any but the freshest slicks may have become viscous and emulsified, may have experienced considerable evaporation, and their asphaltenes and other heavy components may have agglutinated into a discrete particulate phase;[36] the chromatograms of the slick and the source are likely to differ unless the slick is fresh, and the size of the difference will largely depend on the slick's age. Moreover, if the slick is very viscous or emulsified, it will have to be filtered, extracted, heated, and/or dissolved in a non-fluorescing solvent in order to be chromatogramed; while this treatment may not be damaging, it is not helpful to the prosecution's case either. Third, it is not an unmixed blessing that identical chromatograms are invariably produced by crudes from a given area. If all (or even many) Venezuelan crudes give identical chromatograms, and if two or more tankers carrying Venezuelan crude have recently been in the area of a spill, it is not clear how one ship rather than the other could be blamed.

Another simple chromatographic method, paper-strip chromatography, was independently published in 1953 by Herd,[37] who claimed that he had used this method to identify fuel oil that had been spilled in the harbor of Wellington, New Zealand. While Herd was apparently ignorant of Schuldiner's work (in any event, he did not cite it), his claims are strikingly similar, and he asserted that his method "gives visual evidence of complete identity or of non-identity and, if necessary, the strips can be used as evidence in a court of law."

All the reservations that apply to Schuldiner's methods apply just as strongly to Herd's. One further reservation merits special attention: Herd's methods "identify" only the ether-soluble portion of the slick. Although the ether-insoluble fraction of a slick is admittedly difficult to work with in the analytical laboratory, it can provide valuable information (particularly on naturally occurring microsolids); in any event, it does not seem prudent to ignore it altogether because it can be a sizable fraction of the slick. Ludwig & Carter[32] have reported that 12 crude oils contained (on the average) 7.9 per cent ether-insoluble material, that some crudes contained as much as 15.5 per cent ether-insolubles, and that one film of oil collected at a beach near Santa Barbara contained 6.5 per cent ether-insolubles.

Active Tagging

The reader may already have surmised that we have reservations about the validity and efficacy of passive tagging, and he will have been correct. Oil pollution, like the Devil, is said to be legion, and it is no less treacherous to identify absolutely; identification based on passive characteristics seems to be especially worrisome because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized at sea; furthermore, even if these processes do not occur, they create formidable forensic problems for the prosecution, and telling counter-arguments for the defense.

Although God, nature, and geochemistry have not conspired to simplify the forensics of oil pollution, we may, with due humility and caution, come to our own aid. For if the intrinsic components of the oil slick do not lend themselves to reliable identification, we must consider the possibility of introducing additives (active tags) that will suit our purposes. What does one require of an active tag? Ideally, it should satisfy ten criteria.

1. It must be an unusual material that is never found in the environment and is found only in the petroleum to which it has been added.
2. It must be compatible with (i.e., chemically unreactive and physically stable) and soluble or dispersible in the oil.
3. It must be both insoluble and nondispersible in water.
4. It must be relatively involatile.
5. It must be stable to chemical, photochemical, and microbial degradation in the oil-slick environment.
6. It must be easily detectable in extremely small quantities by readily available analytical techniques.
7. It must permit modifications so that when it is added to a particular oil shipment it provides a unique code or "license plate" for that carrier or transporter.
8. It must remain with the oil during the course of its history following a spill.
9. It must in no way interfere with the end-use applications for that oil, nor complicate further processing and refining.
10. It must be available in quantity at economical prices.

While few tags will be ideal, all candidate tags must satisfy all criteria to some degree.

We have investigated two types of oil-soluble tags and one type of particulate tag, and find some (though unequal) merit in each.

Halogenated Aromatics

Over the past several decades, many studies have been performed to identify and characterize the constituents of petroleum. Although many types of aliphatic, aromatic, and heterocyclic compounds have been identified, there is no evidence of halogenated, polynuclear aromatics in crude oils. This class of compounds has many other characteristics that repay careful attention.

First, polynuclear hydrocarbons are (in comparison with aliphatic hydrocarbons) quite stable to oxidation.[38] This stability is due, in part to the resonance and bond-dissociation energies of the aromatic system, whose resonance energies increase markedly as the number of condensed rings increases.[39] Halogenation of aromatic rings has, in common with nitration, sulfonation, and acylation, the great advantage of stabilizing the ring against further attack;[40] it also increases the involatility of the parent hydrocarbon, but (in general) does not affect water-insolubility or oil-solubility.

An important feature of halogenated polynuclear aromatics is that there are many different ways to substitute F, Cl, Br, or I (or their combinations) on condensed aromatic nuclei, thereby providing a large number of specific tagging compounds. Moreover, there are many isomers of each parent hydrocarbon. Depending on the parent hydrocarbon, a large number of mono-, di-, and poly-substituted isomers can be produced with halogens, singly or, *a fortiori*, in combination. The simplest possible example, naphthalene, has two products of monosubstitutions ($C_{10}H_7X$), ten products of monosubstitution ($C_{10}H_7X$), ten products of disubstitution ($C_{10}H_6X_2$), and 14 of the mixed type ($C_{10}H_6XY$), where X and Y are any two halogens. There are 42 known and fully identified polychloronaphthalenes; it is obvious that larger condensed systems (say of six or more rings) offer even more structural isomers for selective halogenation. Even the monochloronaphthalenes have boiling points above 250°C (482°F), and further halogenation raises the boiling point correspondingly; the vapor pressures similarly decline with increasing polycyclic condensation.

The stability of overcrowded halogen compounds (e.g., octachloronaphthalene) has also been demonstrated.[41] In view of the various polycyclic nuclei (and the several structural arrangements that are possible for each) that may be halogenated, and the numerous possibilities for halogenation (involving single or several halogens), it is clear that a large family of coded compounds that can readily distinguished from natural petroleum compounds can be synthesized.

We recall that active tags must be identifiable in the slick even after long exposure to the elements and weathering, which ordinarily increases the concentration of asphaltenes in the slick. Petroleum asphaltenes are polycyclic, comprising mostly aromatic rings[42] in a pericondensed sheet configuration.[43] In general, these asphaltenes might present a considerable background problem. However, the analytical technique suggested for the detection of halogenated active tags should minimize this problem, viz, gas chromatography using an electron-capture detector.

The electron-capture detector is a substance-specific device that is sensitive to certain types of molecules containing electrophilic atoms or groups (e.g., halogens, carbonyls, nitro groups, etc.) and certain condensed-ring aromatics, metals, and the like.[44-53] It has a very low sensitivity for hydrocarbons other than aromatics.[54] Furthermore (and very important), the detector is extremely sensitive to halogen substituents: It can reliably detect halogenated hydrocarbons in quantities as low as 10^{-10} to 10^{-12} gram;[55] under optimized conditions, a projected sensitivity of 10^{-16} gram has been reported.[44] Electron-capture gas chromatography has been used successfully to determine parts-per-billion concentrations of chlorinated insecticides in waste water samples,[56,57] and chlorinated hydrocarbons in air samples.[58]

Since gas chromatography has been used extensively to separate and characterize the components of petroleum and its products,[59, 60] it can be used with reliability and precision to separate the components of an oil-spill sample. Coupled with the extreme sensitivity afforded by the electron-capture detector, gas chromatography can be used to ascertain the presence of an active tag by virtue of the tag's structure and substituents. Detection and identification of the tag can be expedited by reference to a catalog of retention times of the several tagging compounds on a standardized chromatographic column.

When an oil sample is brought in for analysis, the retention times of the various chromatographic peaks of the sample can quickly be compared with the catalog, and the proper component peaks identified. The correlation between chemical structure and column retention times (or elution values) is well documented.[61,62] Halogenated aliphatics,[63,64] heterocyclic compounds, and unhalogenated polynuclear aromatics (as well as inorganic halogens) should not interfere because their retention times (and their detectability by the electron-capture device) will not correspond to the tag's behavior. However, if several peaks should occur near (or overlap) the tag's peak, these particular fractions can be collected and rechromatographed under operating conditions that will give a better separation.

Although nothing is known experimentally about the stability of halogenated polycycles in an oil-spill environment, there are excellent theoretical reasons for believing that these compounds will be stable. In general, aromatic structures are stable to oxidation at ambient temperatures and pressures; halogenation further protects the aromatic nucleus from chemical attack. There are excellent grounds for believing that halogenated tags will be much less reactive than the rather inert condensed aromatics that are naturally present in oil, often in large quantities. Since condensed aromatic compounds are not easily attacked by microorganisms, and since halogenated aromatics are even more stable than the corresponding parent hydrocarbons, there is also excellent reason for believing that the tags will be stable to microbial attack. All of this, however, is theoretical conjecture, not proven experimental fact.

Because of the great sensitivity of the electron-capture detector to halogenated compounds, it should be evident that very little of the tagging material is required to tag a large volume of oil. For example, the largest tankers now on the drawing board will hold 500,000 tons of oil. How much tag must be added to identify such immense cargoes? The theoretical limit of detection by electron-capture gas chromatography is 10^{-12}. Therefore, 0.016 *ounce* of tag is (theoretically) sufficient to tag a half million *tons* of oil. But why push the limit of detectability? Why not allow a safety factor of three orders of magnitude? Why not, indeed, because then only one pound of tag (about one pint) will safely do the job. And "safely" is very safe: One gram of oil slick (about ¼ ounce) will contain one nanogram of tag, and one nanogram of a halogenated aromatic substance is extremely easy to detect by electron-capture gas chromatography.

It is not without interest that electron-capture gas chromatography is several orders of magnitude more sensitive than emission spectroscopy[65] and approximately two to three orders of magnitude more sensitive than ordinary neutron-activation analysis[66,67] (i.e., activation that does not use very fast neutron fluxes.) By combining gas chromatography with mass spectroscopy, the tags can be absolutely identified.[68,69] Just as important, because of the sensitivity of the electron-capture detector, the tag can be used in extreme dilution, and can therefore be added to the oil in amounts which will not interfere with further processing or uses of the oil.

Organometallics

Halogenated aromatic molecules are not the only attractive class of oil-soluble tags. In 1962, a group at the National Bureau of Standards,[70] in collaboration with the American Petroleum Institute, developed a number of stable, oil-soluble organic compounds (mostly organometallics) for use as analytical standards in the spectrographic analysis of petroleum products. The trace elements include Al, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, P, K, Si, Ag, Na, Sr, Sn, V, and Zn; as cyclohexanebutyrates and/or ethylhexanoates, these metals make spectrographic standards that have the following properties: Each is reproducable, stable, nonvolatile, oil-soluble, and compatible with all the other spectrographic standards in this series.

Many of these metals can be detected spectrographically in extreme dilution (parts per million or less), so that one gram could be used to tag a ton or more of petroleum. The 28 compounds that were selected as standards were chosen from an initial list of over 150 candidates; many of the candidates that were rejected as spectrographic standards may still be useful as active tags for oil spills: One of the principal reasons for rejection was extreme chemical purity (e.g., the metal naphthenates), and this requirement might be somewhat relaxed for oil-spill tags. These 28 standard samples, prepared in solid form for easy weighing and handling, may be purchased for $2.00 a gram from the National Bureau of Standards. Obviously, in mass production (with some relaxation of the requirements for extreme chemical purity), the price might be significantly reduced.

Even though all this work on spectrographic standards has made the use of certain organometallics an attractive possibility, there are still several problems and doubts that must be resolved. First among these is the problem of solubility. Only a few of the Bureau of Standard's organometallic standards could be dissolved in oil, without heat or other solvents. If the standard were dissolved in a solubilizing agent (such as a free carboxylic acid, a diketone, or an ester) and then diluted with the base oil, however, the resultant solutions had optimum stability and highest concentrations of trace metal.

The solutions were judged satisfactorily stable if a solution of at least 500 ppm of the trace metal of interest remained "clear and devoid of visible change during several weeks at room temperature." An excellent solubilizer and stabilizer was found to be an equimolar mixture of bis (2-ethylhexyl)amine and bis(2-ethylhexyl)dithiocarbamic acid in an equal volume of xylene. It is not clear, however, what the highest stable concentration of metals might be. A related question is more importat still: What happens to the analytical standard once the solubilizers and stabilizers have evaporated, as is likely after a slick has aged on the sea for several days? Will the standards gel or precipitate?

A second major problem is background: Most crude oils contain traces of inorganics (especially metals), and some crudes have more than 0.5 per cent ash; there are several excellent reviews of the literature on this topic.[13,14] Many refined petroleum products also contain metals, either deliberately added (e.g., components of additives to impeded corrosion and oxidation or to improve lubricating properties), or adventitiously present (e.g., volatile organometallics in the crude that were not removed during refining). How can this background be distinguished from the active tag? Analysis of petroleum shipments for the presence of background interferents is obviously not the answer. It is much too costly, for one thing, and for another there is no guarantee that the metallic suites in the oil slicks will be identical to those in the unspilled oil. Indeed, there is every reason to believe that the suites will be drastically different.

A better solution is to separate the tag from the slick (by chromatography, for example) before attempting further identification. Since the tag is a chemically stable "known," and since the organic moiety of the tag (e.g., cyclohexanebutyrate) should be rare in petroleum, there is no reason to believe that background suites will invalidate this method of tagging. However, separating and concentrating the tag from each slick sample adds to the time and cost of identification; since there are several thousand oil spills in U. S. waters each year, the problem of time and cost is not inconsiderable.

Radioactive Tags

Radioactive isotopes have been examined for possible use in a tagging system, and eliminated for two broad reasons. First, there are not enough isotopes with the right half-life to make the system work and second the use of radioactive material in public places is political dynamite.

Ideally a radioactive tag has a lifetime of 90 days, a reasonable cost, is easily detected, and readily available. Lifetime of all tags should be about the same so that the relative abundance of isotopes does not vary with time. Thus, a minimum tagging system would have 30 or more tags available with half-lives between 70 and 110 days. Of 1700 isotopes examined, 15 have half-lives of 70 to 110 days and, of the 15, a majority were either too expensive or too difficult to detect.

Politically it is not wise to put radioactive material in oil when there is any possibility that the radioactive material might escape into the air or water. Recent experiences in Japan with the visit of nuclear submarines show how sensitive the public is about radioactive contamination of water.

Particulate Tags

Before discussing active particulate tags, it is well to say a little about the particulate material that is naturally found in petroleum. *The* basic reference on this subject is a 1937 paper by J. M. Sanders,[71] to whom all more recent are heavily indebted. In general, the particulate matter in petroleum consists of spores, pollens, fragments of tissue, hairs, microalgae, bits of feathers, etc. In addition, much of the particulate matter is in the form of asphaltenes, which are identified as suspended solids, colloidal particles, or solute molecules, depending on the investigator and his techniques.[43] Although these particles can convey a wealth of information to the careful investigator, their relatively small number and wide variety prohibit their use as particulate passive tags; furthermore, an oil spill may entrain pollens, spores, and other biological matter during its exposure to the elements.[72]

Adding well-characterized particles to oils is a promising technique. In the first place, these particles can be easily manufactured under current technology; second, they can be added to oil in small, measured quantities; third, there is good evidence that, if the need arises, they can be isolated from the oil matrix in quantities sufficient for very specific identification.

Active particulate tags share all the advantages of active oil-soluble tags (viz, specificity and small amounts of tag for proper identification), and offer several other advantages that might make them more suitable. Foremost among these advantages is the ease with which such particles may be produced by one basic technique: grinding and spheroidizing of solids produced from an appropriate liquid melt.

Rather homogeneous solid material can be obtained by: 1. solidification of a liquid melt, 2. coprecipitation from solution, 3. efficient mixing and sintering of suitable solids, and 4. deposition from a vapor phase; almost any such material may then be spheroidized.

We strongly recommend that particulate tags be prepared as microspheres for several reasons: 1. their small surface area per unit volume and lack of areas of large surface curvature make them relatively insusceptible to chemical reactions; 2. these same qualities make it rather unlikely that they will clog or impact upon passage through small apertures, or adhere to interfaces; 3. microspheroids are much more readily sized (e.g., by sieving, sedimentation, and microscopic methods) than any other shape; and 4. the technology for producing them is eminently feasible, and so is the technology for characterizing them.

The flowability of microspheroids makes them ideal for unit operations where mixing is necessarily of importance; flowability is obviously important where trace solids are to be added to a very large amounts of liquid. All these points also apply to simplifying the preconcentration and isolation required in any analysis of suspensoids. Finally, small particles (10-50 microns) are not rare in nature; but very smooth microspheres of this size are much less common.

The most common process for making microspheres is liquefaction of a particle followed by solidification in a dilute, slowly moving gaseous "suspension." Other common techniques are: tabling to produce Lucite spheres; deposition from liquid solution for certain resins; and mechanical action, as when polishing compounds used in ball mills produce ceramic or glass spheres. There are also several methods for makig microspheroids from metals.

Many materials have been made into microspheroids: soft and hard glasses[73-75] (which may be "doped" with a wide variety of metallic salts), metals,[76,77] ceramics, nitrides, carbides, celluloses, starches, polystyrene, phenolic resins, and many other organics.[78] Many suitable microspheres are already commercially available; others can be expeditiously made by custom synthesis. Their costs range from a fraction of a cent a pound (for some commercially available materials) to $1,000 a pound (for custom synthesized rare metal microspheres).

Exact methods for analysis and identification of oil spills that contain particulate tags depend on many factors. A thumbnail sketch of what, at this time, appears to be a reasonable procedure follows:

1. Microspheres of about 10 microns diameter would be produced by spheroidizing a suitable, finely ground and sized solid.
2. These particles would be characterized in preliminary tests to ensure proper quality control over such critical factors as particle diameter, density, content of trace additives, etc.; the data would then be carefully cataloged.
3. The particles would then be metered into the specified petroleum (preferably as it passes through a pipeline or as it is pumped into a tanker). In order to have, on the average, 10^3 particles per liter of oil, only about 5×10^{-4} gram of particles needs to be added to each ton of oil; this amounts to 50 grams for a 100,000-ton tanker.
4. Upon spillage, a representative sample would be taken from the slick; the sample need not be much more than a few liters.
5. The particles in about a liter of spilled oil would then be preconcentrated as follows: 1. centrifugation and washing with a light hydrocarbon; 2. washing with more digestive liquids (perhaps acids or bases); 3. a terminal filtration and wash on a Millipore filter; and 4. transfer of the solids to suitable microscopic mounts.
6. Analysis (as in step 2) to identify the particles. These tests might include microscopy (for size and shape, color, phosphorence, fluorescene), microanalysis (for density, hardness, trace analysis), or microspectrometry (light absorption, fluorimetry, reflectance). Microspectrofluorimetry could provide a characteristic spectrograph of just one or of a number of particles; such a trace would, indeed be a "fingerprint."
7. The data from the preceding step would be compared with the data catalog (see step 2).
8. In the case of a multiple, confluent spill, the individual offenders could be identified readily provided that only one type of tag had been added to each oil. To determine how much of the spill was due to each offender would involve characterizing a larger, representative sample of microparticles; based on the number density of each type of tag, proportional liabilities could be estimated.

Microspheroidal tags permit of a very large number of identifiable forms. Considering only particle sizes of 10-50 microns with an error of ± 2.0 microns for a given size, there are at least 11 distinct and well-defined sizes.[79] For density, given a rage of 0.9 - 1.50 grams/ml and an error of ± 2 per cent, we have, again, at least 11 possible characterizations.[80] The product of 11 sizes and 11 densities is 121 distinct particle types. In addition to these types, particles may contain trace amounts of chemically detectable materials which may be characterized qualitatively or quantitatively. A series of microtests could easily determine whether or not 20 or so readily identifiable trace chemicals are present in the particle.[81-85] With a very simple binary code (in which each of the trace chemicals is merely determined as "present" or "absent"), 20 trace chemicals permits 2^{20} (1,048,576) possible particle characterizations. In combination with the 121 basic particle types, trace-chemical binary coding gives well over 100 million types of identifiable particulate tags.

Addition of Active Tags to Petroleum

The metering of small amounts of liquids has been developed by the chemical, pharmaceutical, and processing industries; ideally, the tags would be injected into the oil as it passes through a pipeline or as it is pumped into a tanker). For the particulate tags we recommend (2-50 micron spheroids), the same techniques will suffice.

Addition of a tracer material to petroleum involves two similar and related critera: First, the tracer should be in a homogeneous phase, and second, this carrier phase should be injected uniformly into the petroleum so that the resulting tagged dispersion (or solution) is also uniform.

There is ample evidence that relatively stable dispersions of particles in a petroleum-based liquid are easily produced. It is important that this stability be maintained when the carrier fluid is injected into the petroleum. Surfactants are critical to stability.[86] In crude oil, enough surfactants (such as porphyrins) are usually present to assure stability (at least for the dilute suspensions we are considering); in refined products, it may be necessary to select the particulate tag with great care so that the appropriate surface properties (hydrophobicity and oleophilicity) pertain. Highly polar materials (e.g., ionic salts) actually stabilize suspensions when the particles are larger than about one micron; the only important exceptions are metal sols, which, however, are stabilized by organometallic molecules.

According to Koelmans, "... a [disperse] system is stable when a crossing of the potential barrier between the particles by thermal motion alone is very improbably;"[84] this potential barrier is about 15 kT for a modestly charged double-layer and is much greater than the usual thermal energies (about 1 kT). This energy difference also applies to particles approaching an interface: Thermal energies cannot overcome the surface potential barrier. Very concentrated suspensions (20-90 weight percentage) may be stabilized by adding small quantities of dissimilar particles;[88] this stabilization technique may be of value in prescribing carrier suspensions.

Once a stable carrier suspension has been produced, it can be metered into petroleum without further problems. Many metering pumps are available at nominal cost; some of these (through mechanical action on a disposable diaphragm, bladder, or flexible tube) do not even contact the metered fluid. Since the volume of the metered suspension or solution may be increased almost at will, pump capacities are not of special importance. Sufficiently stable particle suspensions can be produced and then metered into the petroleum which is to be tagged; since this latter step represents a very large dilution, the resulting suspension is expected to be very stable.

Costs of Particulate Tags

The materials' cost for particle tagging should be quite small. The matrix of the particles will probably be a quite common plastic or glass, and would cost a few cents to a few dollars a pound. The trace materials imbedded in this matrix would cost about the same but would be used in almost negligible quantities. The capital outlay for equipment is more expensive. For instance, laboratory apparatus to produce the microparticles would run in the neighborhood of $5,000. A microspectrofluorimeter with a lens system for single-particle measurements might cost $30,000; however, spectrographic analyses of the desired type may be purchased commercially for about $50 a sample. High quality microscopic equipment would be absolutely necessary; it is available for $4,000 to $20,000.

Costs of Oil-Soluble Tags

Halogenated, polynuclear aromatic hydrocarbons vary enormously in price. While many halogenated benzenes can be bought for under $4 a pound, the halogenated polynuclear compounds can be quite expensive. For example, 9-bromoanthracene costs $1,000 a pound, 2-fluoronaphthalene costs $360 a pound, but 1, 3, 6, 8-tetrachloropyrene costs only $30 a pound.

Even the most expensive of these compounds, however, goes a long way in a tagging system. Approximately 0.001 pounds of tag in 50,000 tons of oil can be detected by electron-capture gas chromatography; even assuming the worst (the outrageous price of $5000 a pound for tagging material), $5 worth of tag would identify 50,000 tons of oil—so that the materials cost for tagging one ton of oil is 10 cents. Obviously, many halogenated tags can be had for a fraction of this extreme price. Excellent electron-capture gas chromatographs can be had for $5,000 or less, so that the capital outlay for detection equipment is not a serious problem.

The organometallic spectrographic standards that the National Bureau of Standards designed specifically for analysis of petroleum products are available from the Bureau for $2 a gram (roughly $900 a pound). These tags are detectable in dilutions of 10^{-5}, so that one gram of tag would identify about one ton of oil. The Bureau's spectrographic standards are exacting in the extreme, and these standards are not mass produced. By relaxing the requiremens for such extreme chemical purity and increasing the production schedule, it seems probable that significant cost savings could be effected. Analytical instrumentation for spectrography is widely available commercially at prices beginning at several thousand dollars, and are standard equipment in most analytical laboratories.

Cost of Active Tagging

Since the amount of tagging material that will be added to a ton of oil—whether the tags be particulate or liquid—is one part in a billion, the cost of the tagging material is low per ton of oil. Assuming the cost of tagging material is $4.53 a pound and one milligram of tagging material is added per metric ton of oil, then the per ton material cost is one thousandth of a cent per ton. Costs of adding the tagging material should be in the same order of magnitude. Including all the quality control, analysis, and service, the actual cost of adding a "license plate" should be less than a few cents per ton of oil.

Feasibility studies and demonstration of the system's efficacy should be run before the operational tagging begins. However, the economics and technology are such that the tagging of oil can begin now.

Tagging Codes

Apart from the type of material used for tagging, "codes" and "tagging profiles" will be involved in the system. Oil shipped into one port will be mixed upon unloading with oil from other tankers and hence the stored oil with its mixture of tagging codes will have its own unique tagging profile at a given time. Oil subsequently loaded onto a tanker will be re-tagged by the unique code assigned to the tanker. Thus, the re-tagged oil will have a new tagging profile whose dominant code will be that of the tanker that last tagged the oil. As a result, any oil or oil slick from a tanker will have an underlying tag noise with a superimposed tanker code. To identify the source—last jurisdiction—of the oil not only must the individual tags be identified but also the relative abundance of each tag.

When an unknown batch of oil is recovered for source identification and analysis is begun, two immediate questions arise: Is this oil spilled from a tanker? Who is the parent corporation? The first question arises because many ships, as opposed to tankers, spill oil, and the second arises because oil is within a corporate jurisdiction much longer than in a tanker jurisdiction. To speed up analysis a special tag would be used to identify all oil ever transported by tanker. Since there are a few very large oil companies, special tags could be assigned to each of the large companies, and smaller companies and independents could be grouped and given a special tag for their group. This would be in addition to the unique tag or code of tags assigned to a tanker. Thus, a quick analysis could answer the question as to whether the oil was ever shipped by tanker and which is the overall company in charge of the oil. If an independent tanker carried the oil this would be readily seen.

It would be very wise in setting up this tagging system to require each ship to tag its fuel oil at a bunkering station. This would eliminate confusion of tanker slicks and ship fuel oil slicks.

Tagging System

Each oil company and each ship would have its own tagging code assigned. Depending on the system, the code could be a unique tag or a code of tags. When a tanker loads an oil cargo, two taggings would take place: one by the loading station and one by the tanker.

Each tanker would have its pre-mixed and prepared code carried in sealed bottles. When loading is to begin, the coding bottle would be placed in the code metering pump and the coded fluid metered into the pipeline ahead of the pumps loading the tanker. The natural turbulence of the process would distribute the tagged material throughout the oil. Simultaneously the loading station would tag the oil with its own tag. A sample of the tagged oil would be taken for quality control and for subsequent comparisons with spills.

At each unloading, the oil from the tanker would be sampled and then tagged by the shore facility. The sample would be analyzed for quality control and for the record in case of a spill claim. Tagging during unloading would cancel the tanker profile and eliminate the possibility of false claims against the tanker for oil subsequently spilled.

Tampering with the tagging system would be difficult because tagging is difficult to do except during loading and unloading because thorough mixing is necessary. Furthermore, since a variety of tags are involved, it will be difficult to alter a batch of oil without its being obvious. Sophisticated analysis of the tags can be used to show that some of the tags are spurious. In other words, different batches of the same tag can have subtle differences that can be detected.

Conclusions

We have critically examined two approaches to identifying oil spills: passive tagging and active tagging. Passive tagging is a convenient circumlocution for no tagging at all: Nothing is added to the oil; the slick itself must provide all the evidence for its identification. Active tagging involves adding some known and readily identifiable material to the oil. The added material must satisfy several criteria: It must be soluble or dispersible in oil and insoluble and nondispersible in water; it must be chemically and physically stable in both spilled and unspilled oil; it must not interfere with the refining or with the commercial uses of petroleum; and it must not be too expensive. Two figures of speech are helpful in distinguishing active tagging from passive tagging: Passive tagging amounts to a "fingerprint," active tagging amounts to a chemical or physical "license plate."

Passive tagging does not seem promising, for the fingerprint is likely to be altered or to disappear as the slick is exposed to the abundant sources of chemical and physical energy in the sea and sky. The easily identifiable passive tags of petroleum (e.g., isotope ratios and trace metals) cannot be assumed to be stable in the slick—indeed, there is little doubt that they are unstable—and the more stable passive tags in the slick (e.g., heavy aromatic and alkylaromatic hydrocarbons) are prohibitively difficult to separate and identify.

Active tagging, however, offers several attractive possibilities. Making a good license plate seems much easier than finding a good fingerprint. We have examined two types of tags: oil-soluble tags (organometallics and halogenated aromatic polycycles) and particulate tags (coded microspheroids). Several promising organometallics have been developed by the National Bureau of Standards in conjunction with the American Petroleum Institute; these compounds sell for $2 a gram, they are detectable in parts per million, and they seem to have all the properties of good active tags (compatibility with oil, solubility in water, chemical and physical stability, and ease of identification). The halogenated polycycles have never been used for analytical tracing in petroleum; consequently, no direct experience recommends them. However, they should have many desirable properties, and chemical theory recommends them. Their cost can range from a few dollars to a few thousand dollars a pound, but they are very readily detectable in parts per billion by electron-capture gas chromatography.

Although the feasibility of particulate tags has not been demonstrated in oil spills, coded microspheres appear to have exceptional promise: Many are already commercially available at very low prices; an astronomic variety of coded microspheres can be cheaply and easily made by custom synthesis; and all the particulate tags can be quickly separated from samples of slick and readily identified by available analytical techniques.

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Remote Sensing Of Oil Slicks

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Abstract

An overview of remote sensing methods is presented and illustrated with data taken at the Santa Barbara oil spill. The conclusion is reached that such methods possess monitoring capability but so far the ability to identify the slick material as oil has not been demonstrated. The advantages and disadvantages of each method are briefly discussed.

The tragic consequences of major oil spills, such as at Santa Barbara, are well known. The lesser but more frequent spills probably have equally tragic, if less dramatic, consequences in the long run. While major emphasis is on prevention and control of all spills, as it should be, a reasonable effort must be placed on the development of early detection systems. To this end, the FWPCA and other Federal agencies are investigating the applicability of remote sensing. Within the FWPCA there is interest in earth-bound and in airborne systems and the advantages of a satellite system are not overlooked. Earthbound instrumentation would be deployed in areas of high frequency or high probability of spills such as in harbors and near oil rigs. Airborne instrumentation, on the other hand, would allow occasional spot checks of other areas and effective monitoring of cleanup operations. Ideally, such instrumentation should be capable of detection, identification and of providing areal and thickness measurements. Remote sensing appears to have potential here and the purpose of this paper is to present an overview of these methods along with some experimental results.

Present remote sensing methods are based on the electromagnetic properties of matter. These properties are wavelength dependent, that is spectrally distributed, and in principle this dependence is uniquely related to the chemical species and the physical state of the oil film. Specifically, spectral absorption, reflectance, emission and/or scattering are the relevant properties with present emphasis on the wavelength range from 0.3 microns, in the near ultraviolet up to about 0.8 meters in the microwave region. The corresponding sensors or sensor systems vary from simple optical to very sophisticated electronic equipment as pointed out in Figure 1.

Passive Methods

Passive methods utilize naturally occurring radiation. In the range 0.3 to about 3 microns these methods sense the reflected energy from the sun and sky. A target is detected where a difference in reflectivity between target substance and neighboring scene points exist. These differences in reflectivity result in tonal or color contrast for photographic sensors and output voltage contrast for electronic sensors.

Panchromatic film or sensors do not respond to differences in quality of reflected energy and as a result, identification of slick material does not appear feasible with such devices. In fact, it is possible that no contrast is observed even when spectral differences in reflected radiation do exist. Figure 2 is a panchromatic photograph taken over the drilling platform at Santa Barbara during the oil spill of early 1969. The highly reflective material near the platform is due to dispersant and not to oil which is practically invisible in this picture. However, it should be pointed out that this picture, as all others presented here, was taken directly over the target resulting in minimum reflectivity. The reflectivity of films increases at oblique angles,[1] however, sun glint (glitter) can be a problem at these look angles usually leading to poorer quality photographs.[2]

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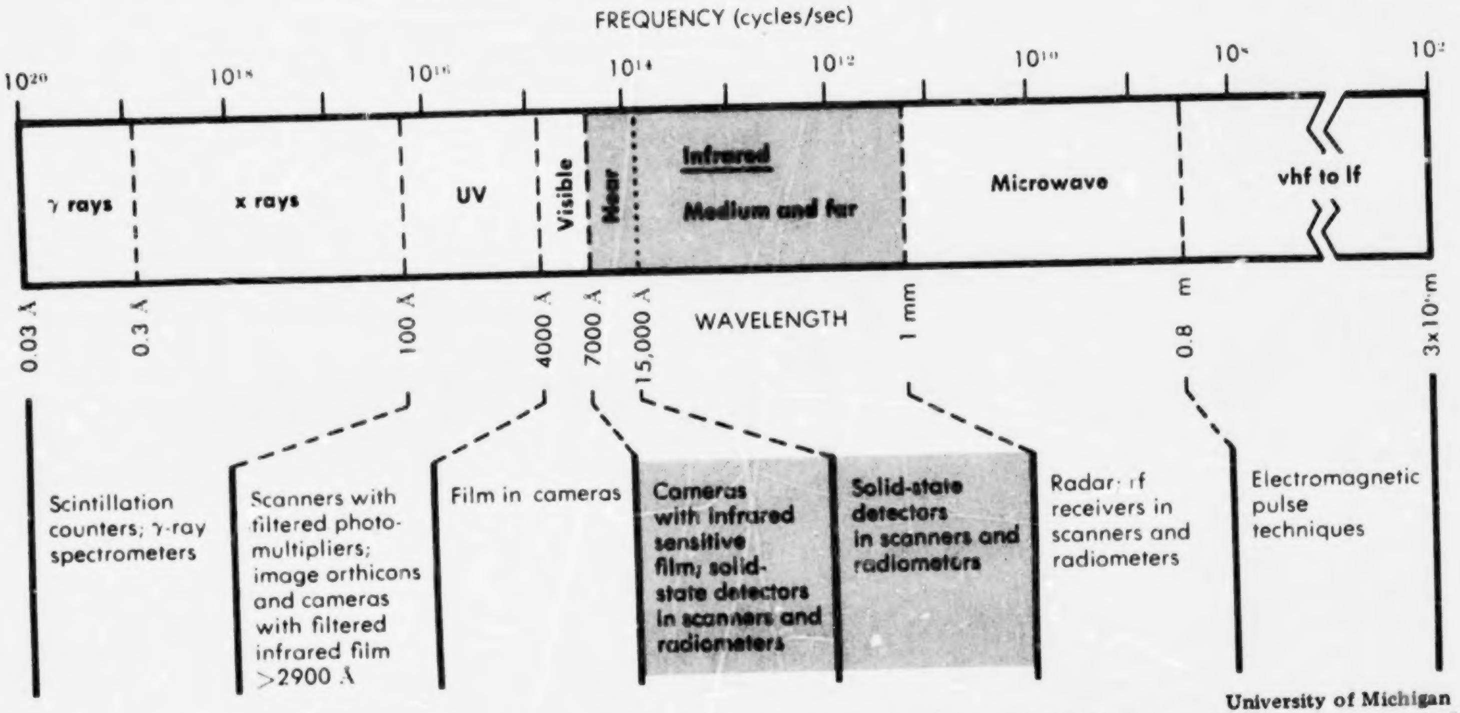
[1] Superior numbers refer to literature references at conclusion of text.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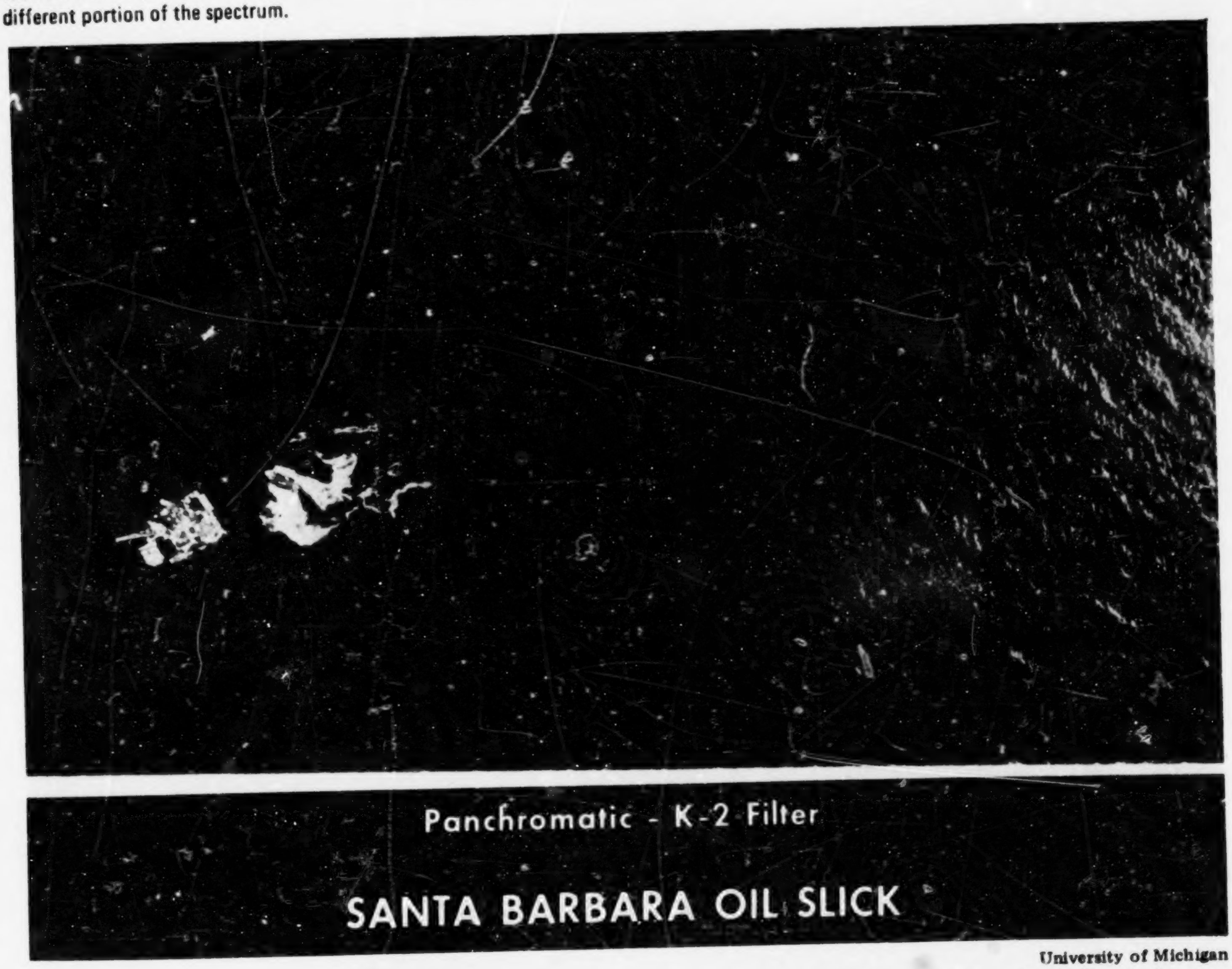
x rays
UV
Visible
Near
Infrared
Medium and far
Microwave
vhf to lf
0.03 Å
0.3 Å
100 Å
4000 Å
7000 Å
15,000 Å
WAVELENGTH
1 mm
0.8 m
3x10⁵ m
Scintillation counters; γ-ray spectrometers
Scanners with filtered photo-multipliers; image orthicons and cameras with filtered infrared film >2900 Å
Film in cameras
Cameras with infrared sensitive film; solid-state detectors in scanners and radiometers
Solid-state detectors in scanners and radiometers
Radar; rf receivers in scanners and radiometers
Electromagnetic pulse techniques

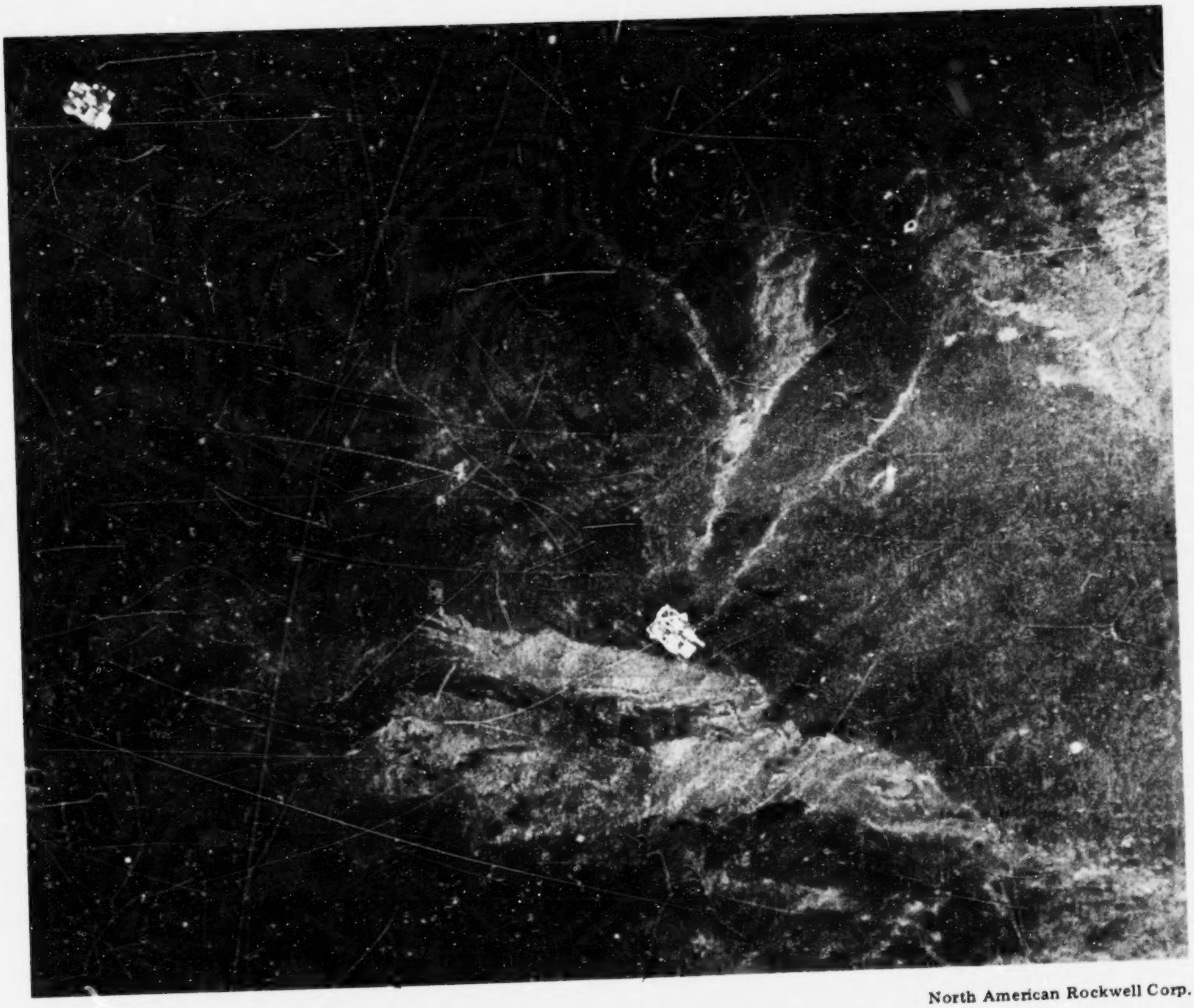
University of Michigan

Figure 1. The electromagnetic spectrum and some sensors that use it. The infrared portion of the spectrum, though much wider than the band of visible radiation, is still a small part of the total. Recent research has focused on the integrated use of several sensors, each making use of a different portion of the spectrum.


Panchromatic - K-2 Filter
SANTA BARBARA OIL SLICK

University of Michigan

Figure 2. A black and white panchromatic photograph taken over Santa Barbara. The highly reflective material near the platform is dispersant. There is very little, if any, indication of an oil film. Photographs taken at other than vertical look angles are frequently of poor quality due to sun glint as seen at the right of photograph.



North American Rockwell Corp.

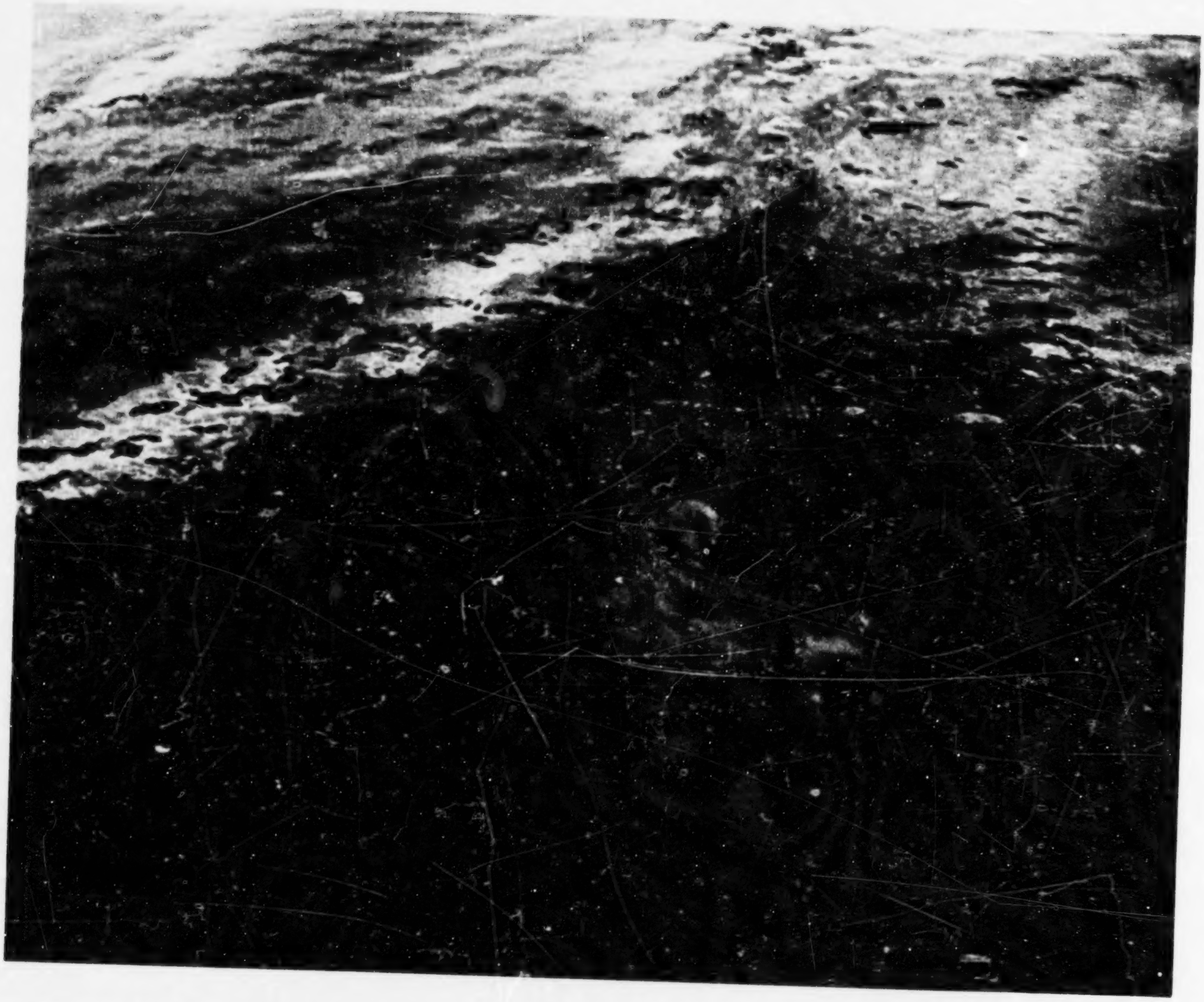
Figure 3. Photograph taken at Santa Barbara. Films of varying thicknesses are shown.

Color photography offers an additional dimension. Figure 3 is a regular color photograph taken at Santa Barbara. Areas of thick oil film show as a grey-brown against the blue-green ocean. Areas of thin film are evidenced by the interference rings typical of such film slicks as in Figure 4.

The spectrozonal technique, an adaptation of color separation photography, provides somewhat greater discrimination than the usual color photography. A three or four lens camera takes simultaneous black-and-white transparencies in selected bands from .36 to .9 microns. Simultaneous projection through suitable filters produces a composite color image. Manipulation of filtration and channel intensity allows enhancement of density differences and consequently, greater target discriminating ability.[3] However, photography in general does not have the on-line feature required for rapid detection and at best provides data for post evaluation of cleanup procedures.

Multispectral methods divide the spectral range into many channels to fully utilize the differences in spectral reflectivities for target detection and identification. The University of Michigan system couples an optical-mechanical scanner with a spectrometer for the visible and near infrared region and utilizes filters in the far infrared.[4] Scanners, utilizing electronic detectors, allow a variety of outputs including black-and-white and color imagery and lend themselves to on-line data processing. Figure 5 illustrates the basic scanning procedure and the operation of a simple device

A schematic of the University of Michigan system, including instrumentation for automatic processing of scanning information, is shown in Figure 6 and examples of single scans are shown in Figure 7. Note the calibration signals generated by internal sources which allow quantitative estimation of experimental signal levels. Eight channels of imagery taken at Santa Barbara are shown in Figures 8 and 9. It can be seen that the lighter tones of the oil slick in the ultraviolet (0.32 to 0.38μ) become darker in the 0.8 to 1.0 microns channel decreasing the contrast. Careful densitometric measurements on imagery such as this provide a reflectance spectrum which has the potential of being identified as that of oil and possibly even the type of oil. Some idea of the discriminating ability may be



North American Rockwell Corp.

Figure 4. Natural color photograph taken over Santa Barbara. Interference fringes may be seen indicating the presence of thin films.

obtained from Figures 10 and 11. In Figure 10, the oil slick reflectance in the U.V. is contrasted with the absence of significant differential reflectance in the solar infrared. In Figure 11, the lower reflectance in the U.V. of kelp compared with water is contrasted with the exact opposite effect in the solar infrared. It is possible to implement such recognition techniques by on-line data handling systems when electronic multispectral scanners are used.[5] In fact, this is a major advantage of scanners.

In the longer wavelength regions from 3 microns to .8 meters, the detected radiation is that emitted from all objects which are at temperatures above 0° absolute.

In the infrared region, the total radiated power from a black body (ideal radiator) is given as $W = E\sigma T^4$ where σ is the Stefan-Boltzmann constant, T is the absolute temperature, W is the emitted power and E is the emissivity which for a black body has a value of 1. An infrared sensor (or radiometer) measures the emittance (energy emitted per unit area) from the scene elements. These measurements are interpreted as apparent surface temperatures of those elements, by assuming black body emissivity. Because all natural objects have emissivities less than 1, the apparent infrared radiometric temperatures will always be less than the thermometric temperature. In any case, contrast between target and background results from differences in emittance.

Infrared scans may be processed to provide imagery as illustrated in Figure 12 which was taken at night over Santa Barbara. The dark areas represent portions of the oil slick having apparent temperatures less than the surrounding water. The interior regions of the slick appear bright, indicating a higher apparent temperature. The explanation for this is not presently known. Either differences in emissivities, differences in local temperatures or both may be the cause. The evaporation process or heat conduction anomalies could result in temperature differences which depend on film thickness.

The relationship of emissivity to film thickness is presently being investigated.[6] The North American Rockwell group 7 made measurements on a 7.5 gallon dump to determine the variation in total emittance with thickness. Microdensitometer tracing of the IR imagery provided an isodensity trace, Figure 13, which was related to the thickness as shown in the figure. Thus, microdensitometry of IR imagery or on-the-line processing of individual scans may yield satisfactory film thickness measurements.

Like the infrared sensors, microwave radiometers respond to total emittance which, in turn, depends upon the emissivity and temperature of the body of interest. In this region, emittance is related to temperature by the expression $W = E\ T$. Assuming that E has a value of 1, the emittance provides a direct measure of T, which is referred to as brightness temperature. Differences in brightness temperature result in changes in the radiometer voltage output which may be converted to an image in the same manner as the IR signals. It is known that the state of polarization of the emitted radiation varies with look angle. As a result, it is common practice to separately measure brightness temperatures from both vertically polarized and horizontally polarized radiation. In general, the vertically polarized emission is larger than the horizontally polarized.[2] Here, as in other methods, differences in the sensed parameter allow detection.

Figure 14 shows a microwave response curve compared with an IR microdensitometer trace of the same flight path. The microwave response indicates greater brightness temperature in those regions showing cooler temperatures in the IR region. Measurements made from a causeway revealed a similar picture. The distinct difference between the IR and microwave is at first startling; however, emissivities in these two regions may be quite different accounting for the opposite results..

As in the IR, film thickness apparently has an effect on the emittance. Aerojet General[8] has performed laboratory measurements along these lines. At present, it appears that the microwave region offers little possibility for identification but has definite potential for detection and thickness measurements.[8, 9]

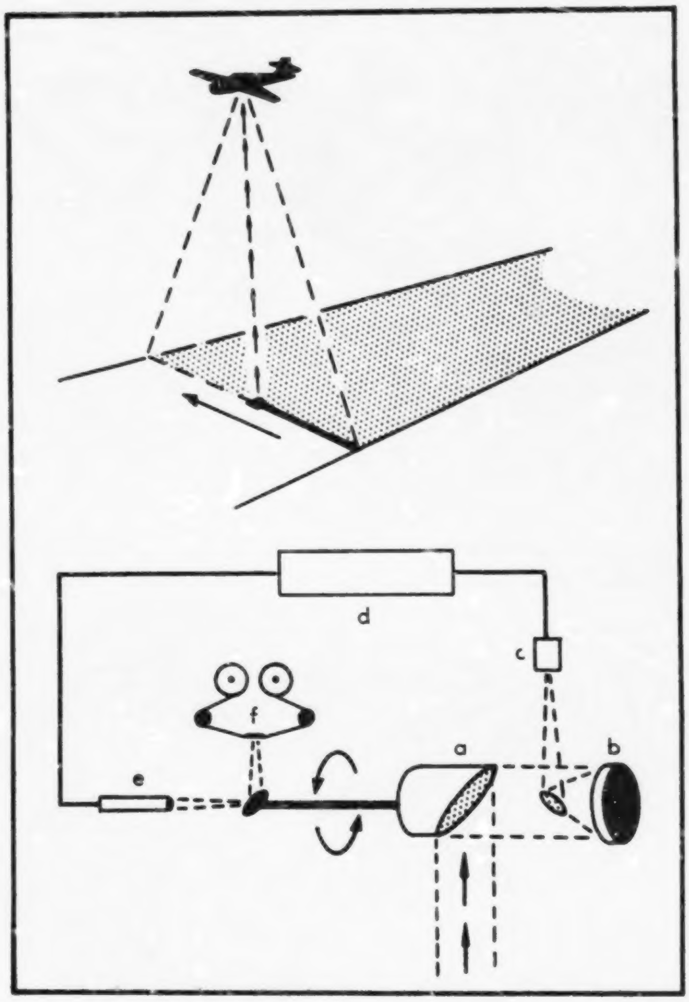


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Figure 5. The top figure illustrates the scanning procedure and the bottom figure illustrates a basic scanner. In the bottom figure (a) is a rotating mirror, (b) is a concave mirror, (c) is an electronic detector, (d) an amplifier, (e) a light source modulated by the amplifier output, and (f) is photographic film for image registration.

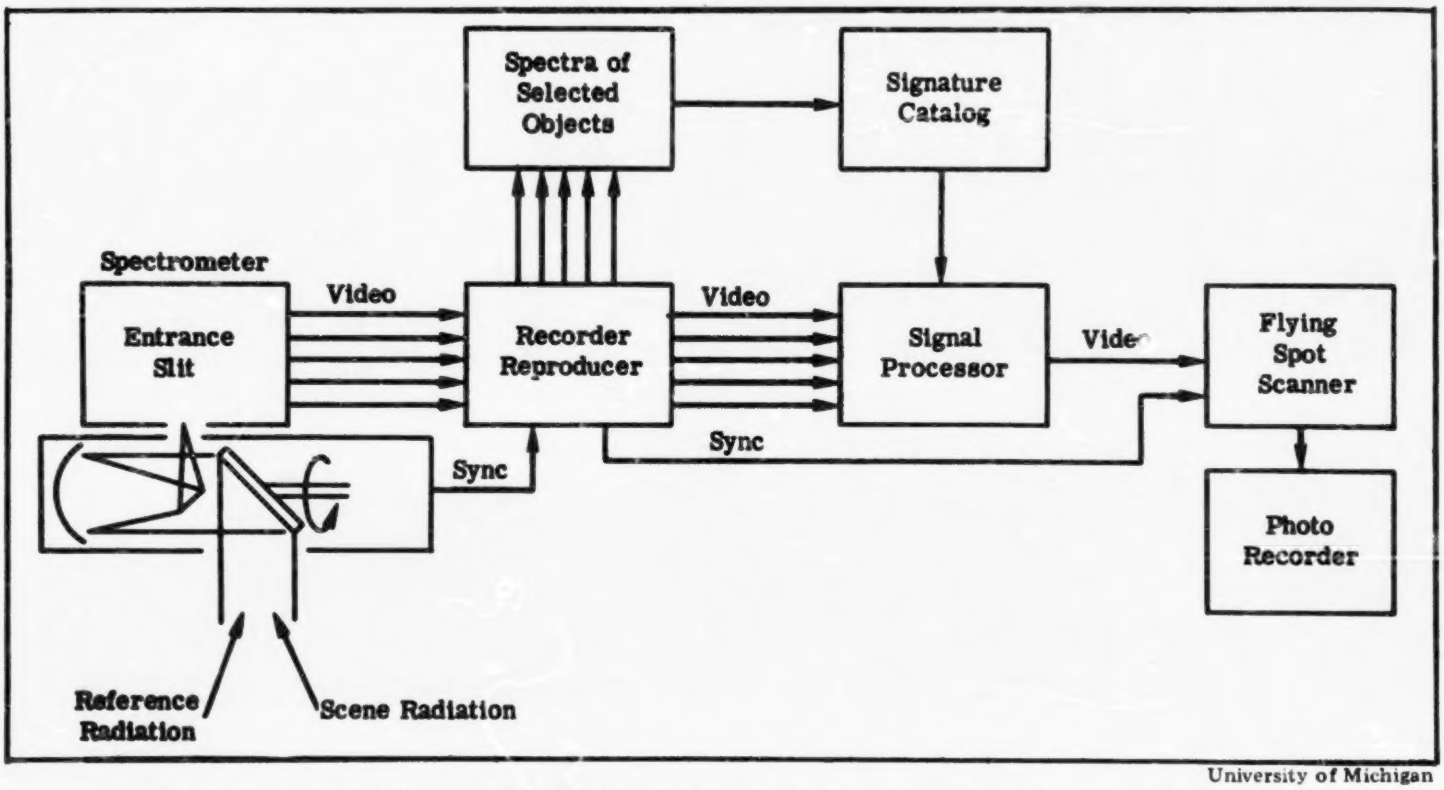

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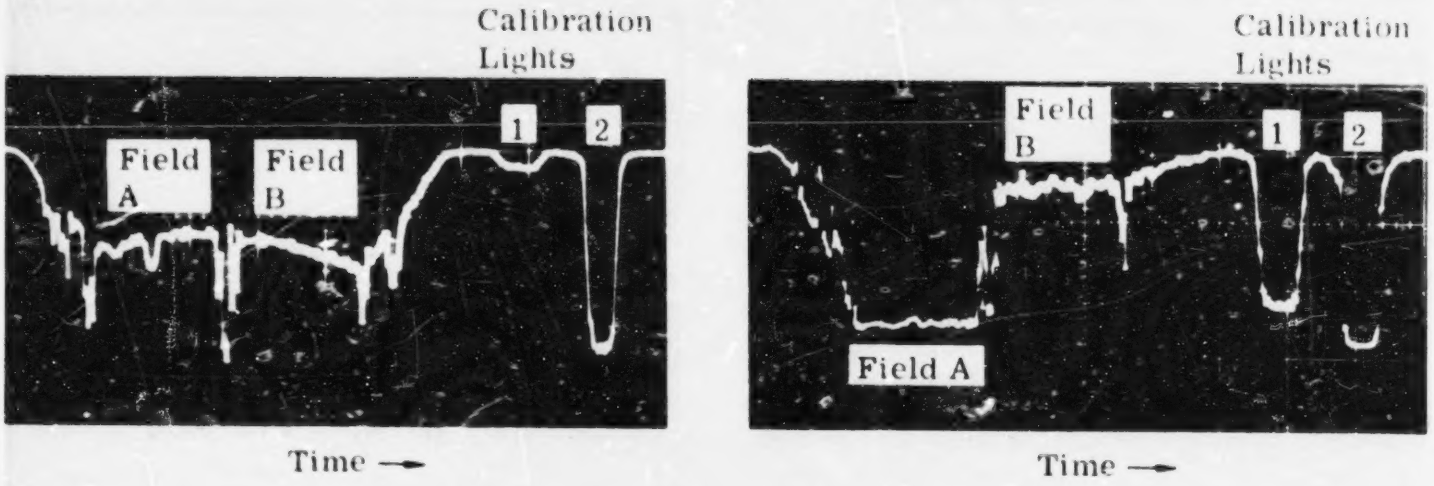
Figure 6. A schematic of the University of Michigan multispectral scanner and associated data processing equipment.



University of Michigan

Figure 7. Single scans from a multispectral scanner. Internal sources supply calibration signals (1 and 2). Field A and field B have different spectral characteristics. Typical spectrometer video data (U). California Rice Fields 5/26/66 at 1400 hours.

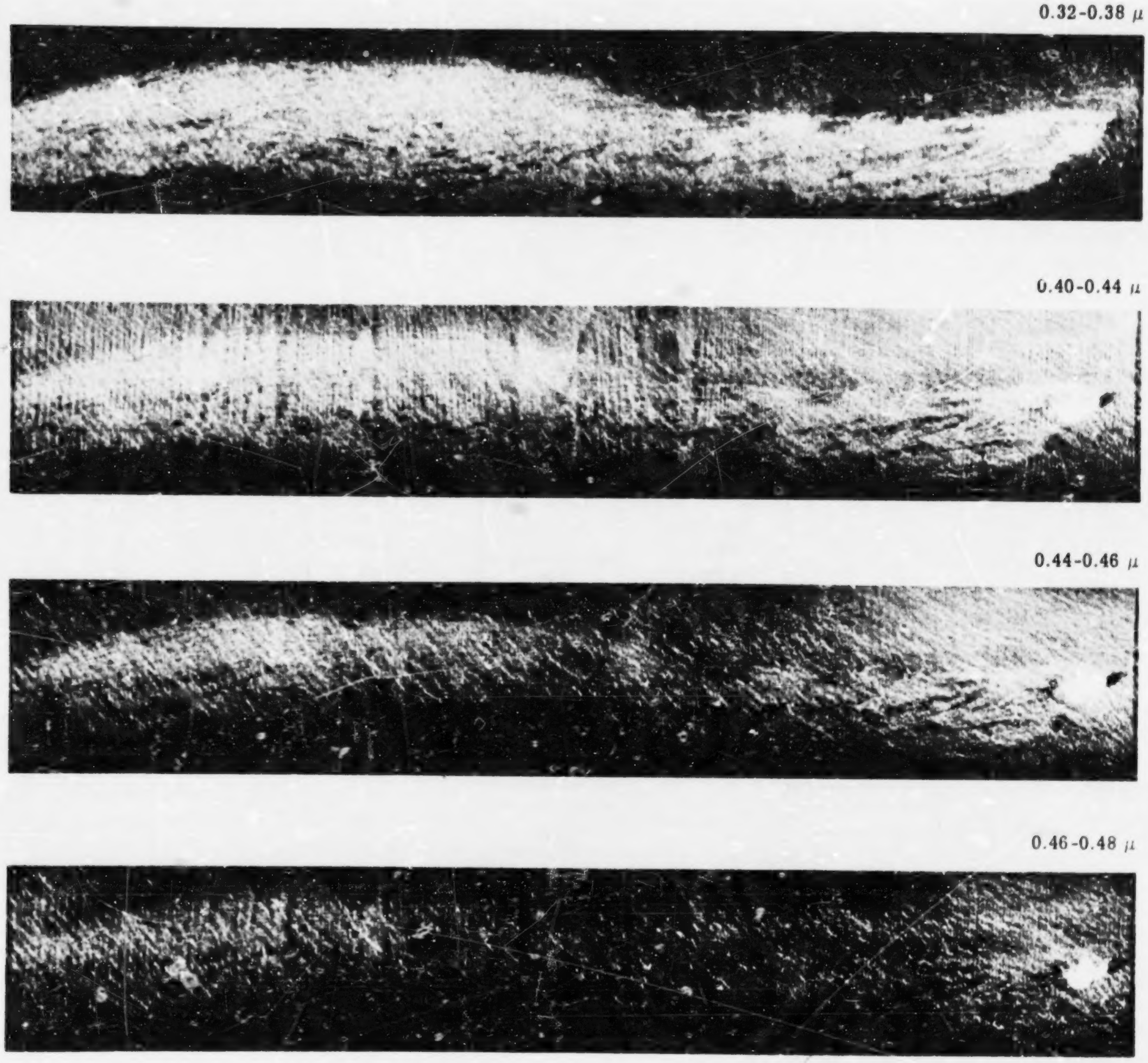


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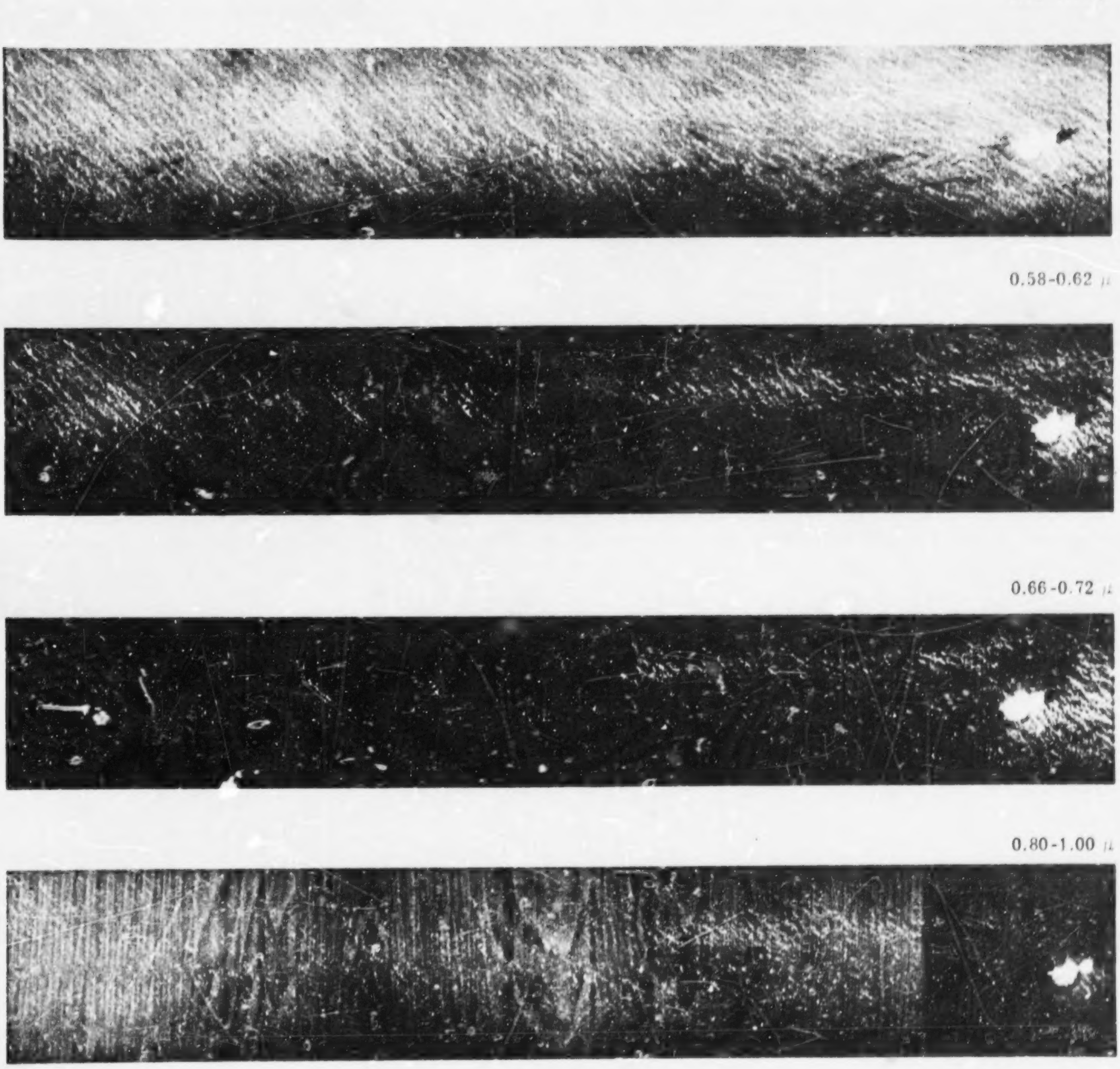
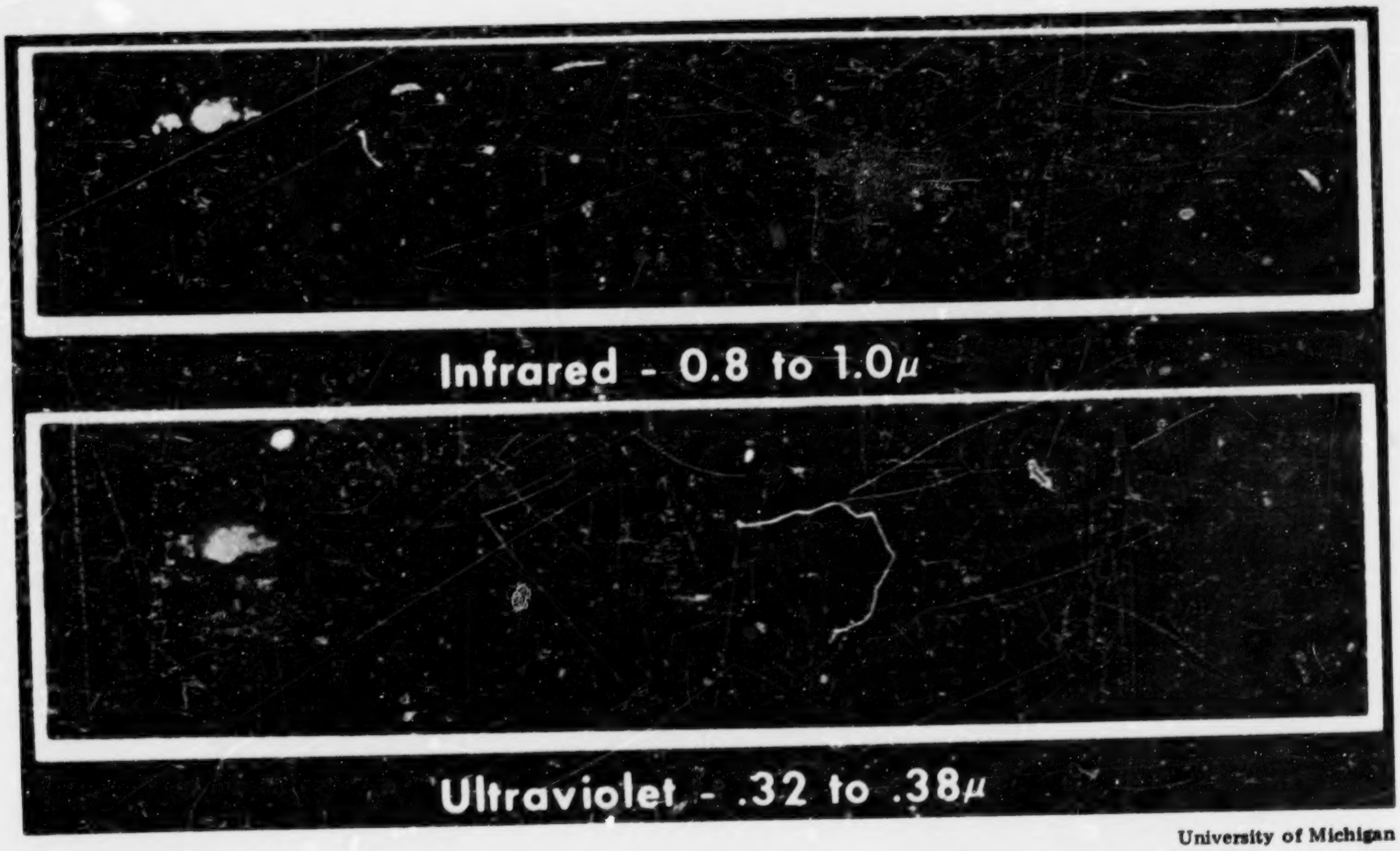
Figure 8. Four channels of University of Michigan multispectral imagery. The spectral range is from 0.32 to 0.68 microns. Note decreasing contrast from top to bottom.


0.52-0.55 μ
0.58-0.62 μ
0.66-0.72 μ
0.80-1.00 μ

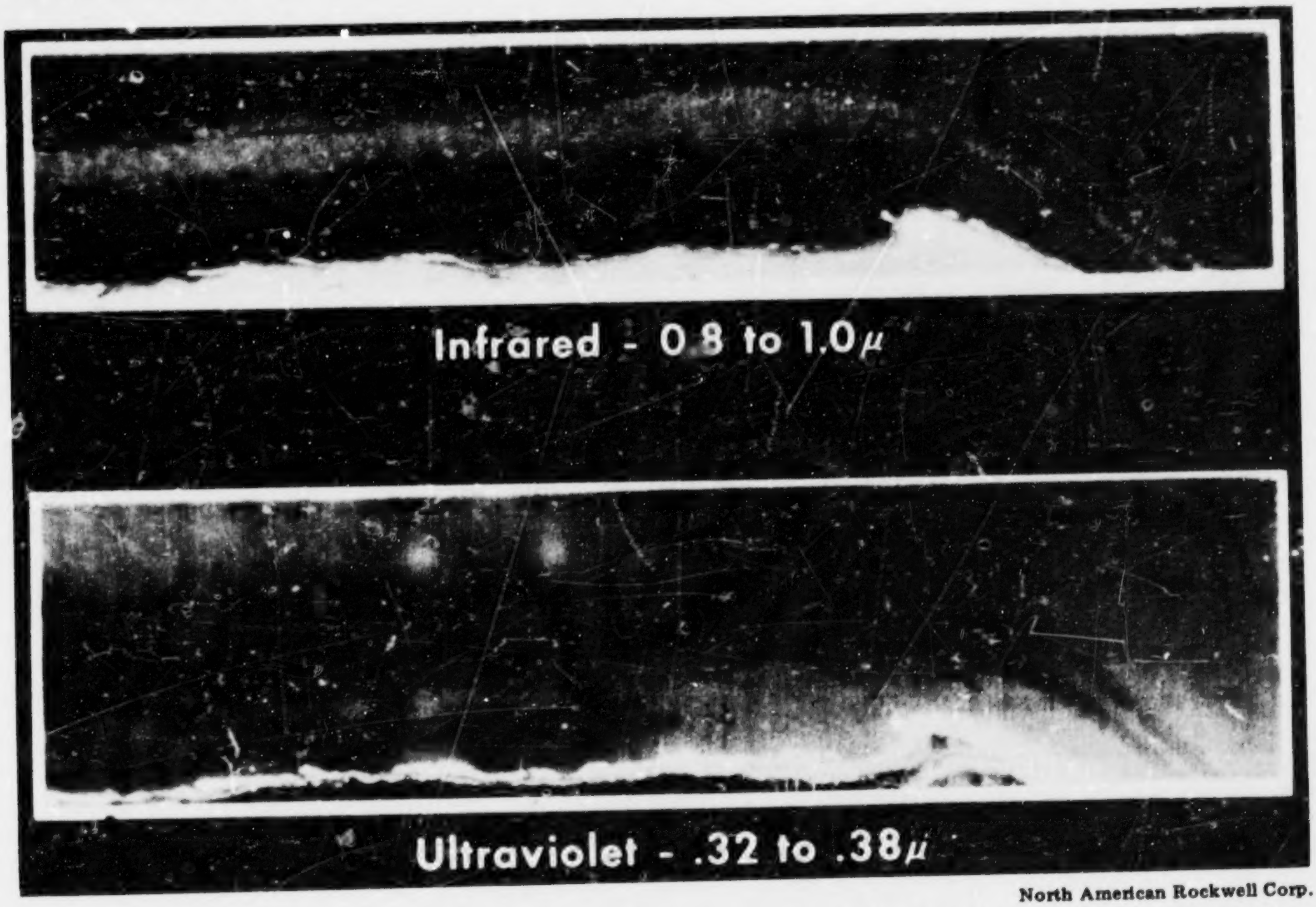
University of Michigan

Figure 9. Four channels of University of Michigan multispectral imagery. The spectral range is from 0.52 to 1.00 microns. It is almost impossible to detect oil film in this set.


Infrared - 0.8 to 1.0μ
Ultraviolet - .32 to .38μ

University of Michigan

Figure 10. Two channels of imagery with oil on the surface. In the solar infrared at the top no trace of oil is seen, while in the U.V. at the bottom, the oil shows up clearly.


Infrared - 0.8 to 1.0μ
Ultraviolet - .32 to .38μ

North American Rockwell Corp.

Figure 11. Two channels showing fronding kelp. In contrast to oil the kelp is highly reflective in the solar infrared and absorbing in the U.V.

Another passive method which appears to have potential but has not been field tested in oil slick detection is the Fraunhofer Line Discriminator, used to sense solar stimulated fluorescence. Many substances, including oils, absorb light particularly in the ultraviolet region and re-emit this energy at longer wavelengths. The wavelengths of re-emission are uniquely determined by the emitting substance, as are the wavelengths absorbed. Unfortunately, the low intensity of the fluorescence is ordinarily masked by the high intensity solar radiation. The Fraunhofer Line Discriminator takes advantage of the fact that certain spectral lines are partially absorbed in the outer portions of the sun and appear at low intensities at the earth. These regions of low intensity allow detection of fluorescence at these wavelengths even in the background of high overall solar intensity. Hemphill[10] of the U.S. Geological Survey is doing work in this area and it should soon become available for field trials.

Active Methods

Active methods in which the source of radiation is an integral part of the instrumentation, as in radar, have not been directly investigated for use in oil spill detection and identification. However, it is expected that some experiments will be conducted in the near future.

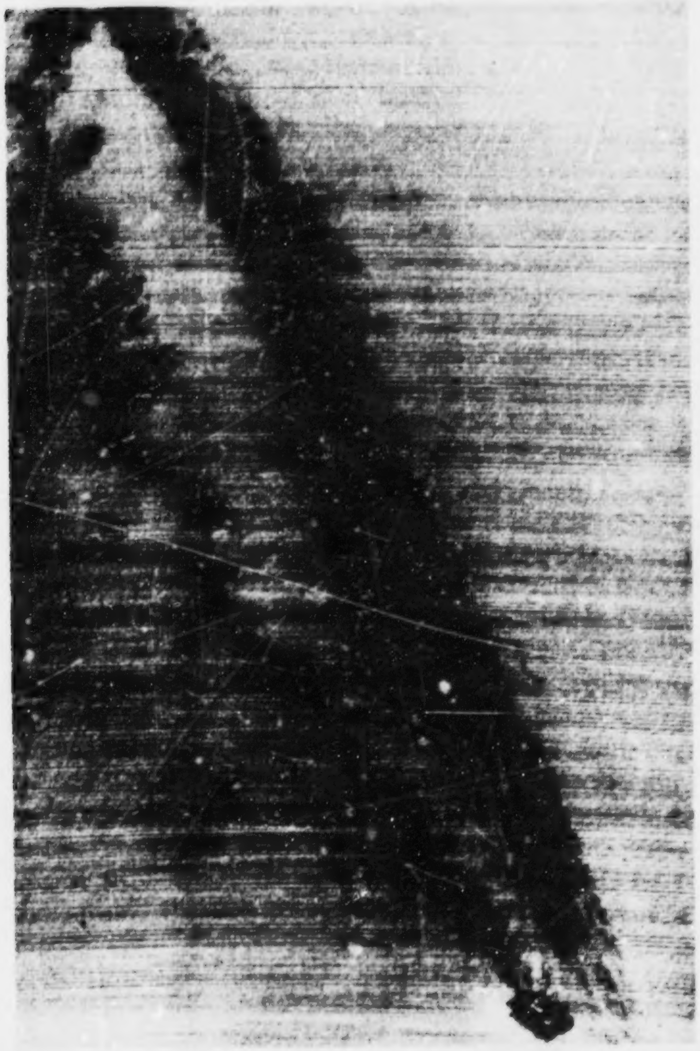


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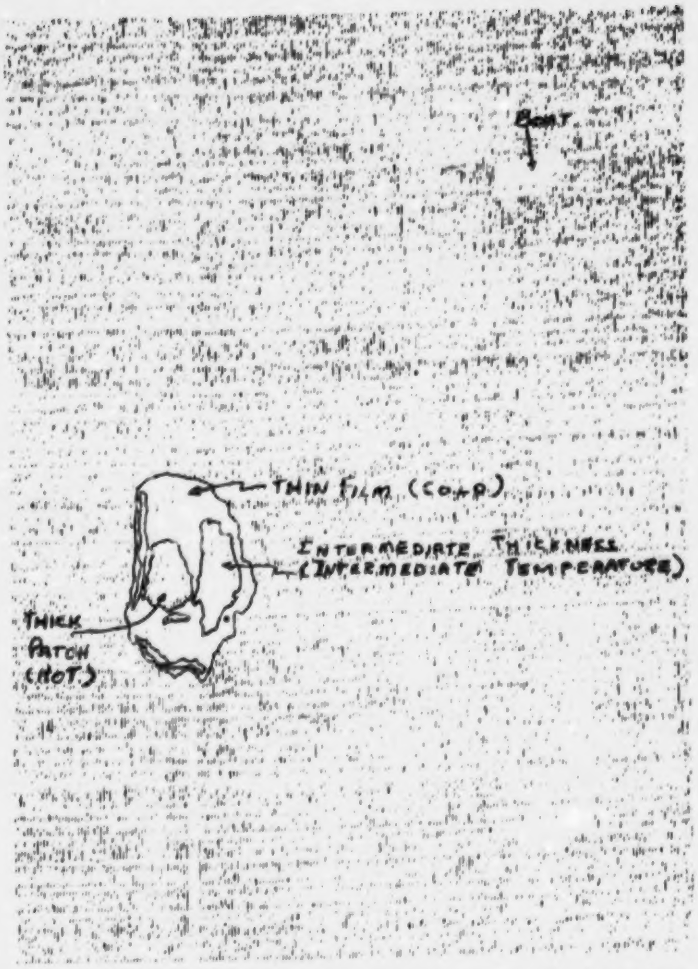
Figure 12. Infrared night-time image (8-13 μ band) taken over Santa Barbara, Platform A, March 27, 1969. Note scan lines due to infrared scanner. Dark areas are thin edges of the oil while the lighter area, between these edges, is due to thick body of oil.



North American Rockwell Corp.

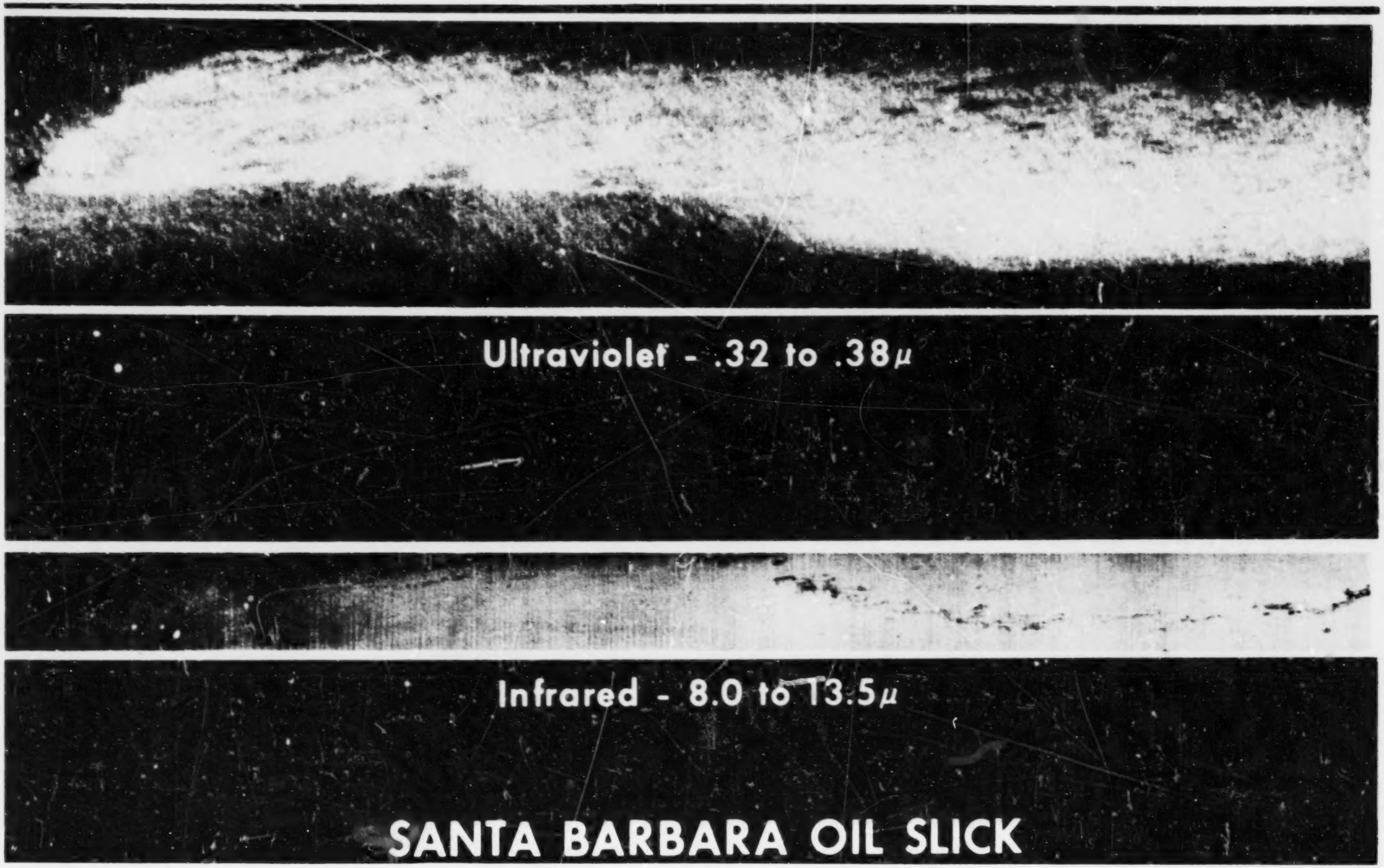
Figure 13. Microdensitometer tracing of infrared imagery of a 7.5 gallon oil dump off Coal Oil Point on March 24, 1969. Lines indicate isodensity contours separating thin areas from thick areas. On original imagery the thin areas are dark and the thick areas are light.

The use of lasers in a radar like configuration is also being investigated. Laser stimulated fluorescence may be sufficiently intense to detect material at night and possibly even in the presence of sunlight.

Conclusions

All methods investigated so far have the ability to detect the presence of a surface film. However, the potential for positive identification of the film substance appears to be offered by multispectral methods only. Unfortunately, the methods (U.V. through IR) by which spectral signatures are detectable become inoperable at night and/or in bad weather. On the other hand, microwave methods possessing all weather capability do not allow spectral differentiation. It may be that other recognition techniques are possible but if so they have yet to be worked out.

A more complete picture of remote sensing of oil spills will emerge after active and fluorescence detection methods have been fully investigated. These sensors will most likely have the capability of detecting and monitoring surface films but not of identifying the contents of the films. Nevertheless, we will have a choice of sensors useful under a variety of situations for detecting films with identification reserved for the laboratory.


Ultraviolet - .32 to .38μ
Infrared - 8.0 to 13.5μ
SANTA BARBARA OIL SLICK

University of Michigan

Figure 15. Compares scene taken in the U.V. to the same scene in the thermal infrared.

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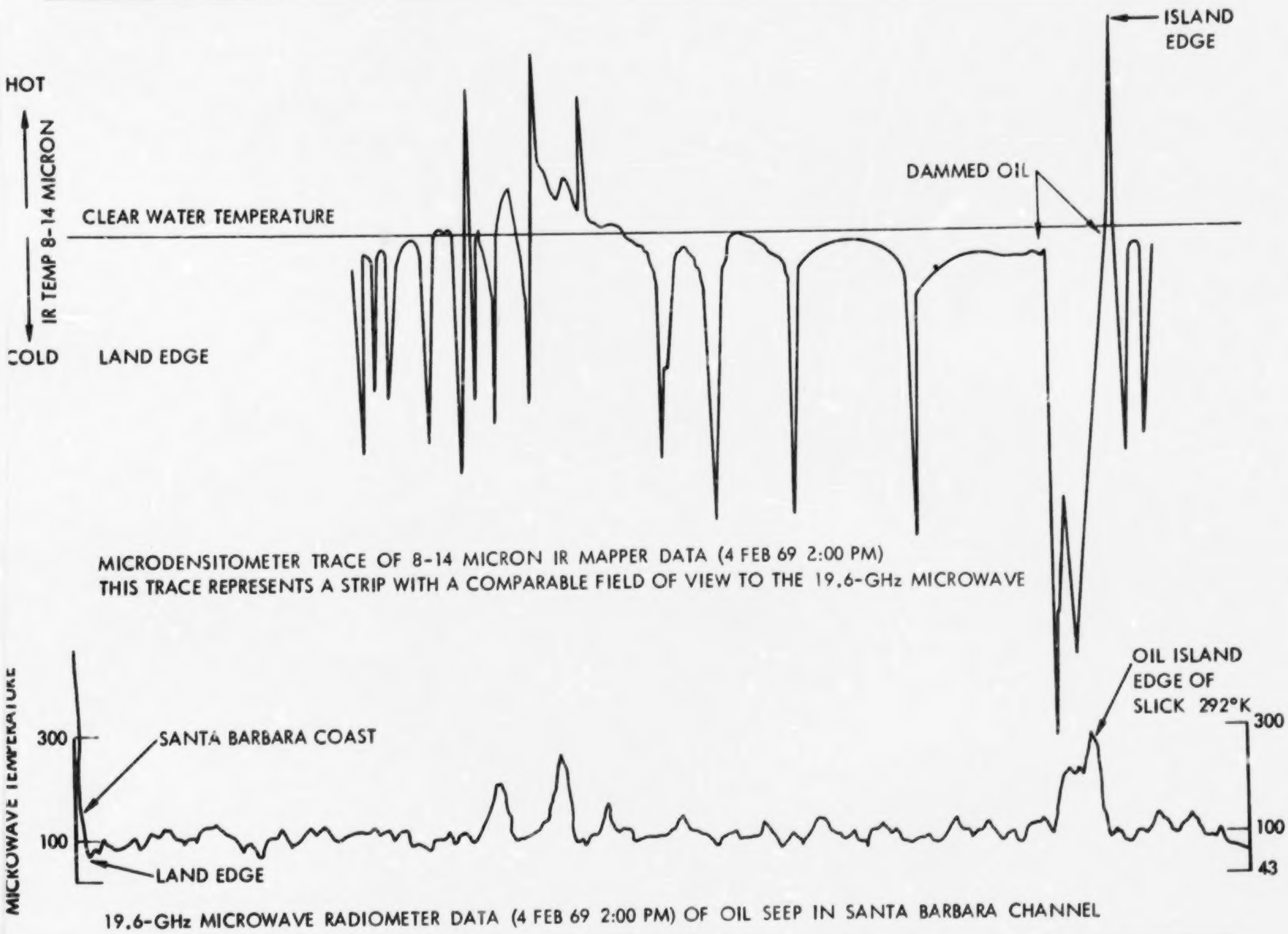

MICRODENSITOMETER TRACE OF 8-14 MICRON IR MAPPER DATA (4 FEB 69 2:00 PM)
THIS TRACE REPRESENTS A STRIP WITH A COMPARABLE FIELD OF VIEW TO THE 19.6-GHz MICROWAVE

19.6-GHz MICROWAVE RADIOMETER DATA (4 FEB 69 2:00 PM) OF OIL SEEP IN SANTA BARBARA CHANNEL

North American Rockwell Corp.

Figure 14. Comparison of microwave and infrared measurements along the same flight path of the Santa Barbara spill. Slick edge images as hot in microwave and cold in infrared. Differences between these data are not yet understood.

The Santa Barbara Study

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Abstract

This paper gives an outline of the unique problems associated with determining the effects of the oil spill in the Santa Barbara Channel and a general outline of biological studies associated with the spill.

The blowout at the Union Oil Well Platform A occurred on January 28, 1969. While flow from the well was stopped within three weeks of the mishap, oil still continues to leak from the area around the well. Present estimates of seepage are around 400 gallons per day. Estimates of seepage from the Coal Oil Point area are around 900 gallons per day. While this means that the man-made seepage is at present only adding a relatively small amount to the volume of natural seepage in the area, it is releasing oil which is intermittently polluting beaches.

The well is located 3 miles offshore from Santa Barbara (Figure 1). Data supplied by the Coast Guard showed that most of the mainland shores of the Santa Barbara Channel and some areas of the Channel Islands were effected by oil by March 31. By the end of July, there was no mainland beach in the Santa Barbara Channel which was uneffected by oil. While the distribution of the oil on the beaches varied, it tended to accumulate in the upper littoral zone.

Prior to the Santa Barbara spill, the *Torrey Canyon* wreck and the *Tampico* wreck were the most publicized oil spills. These differed from the present spill in that the vessels were carrying crude and diesel oil respectively and in both cases the oil was released over a relatively short period of time compared with the Santa Barbara spill. The *Torrey Canyon* spill effected large areas of the shores of England, Wales and France while the *Tampico* spill was confined to a small bay. The *Torrey Canyon* spill was heavily treated with detergents while detergent use was negligible in the Santa Barbara Channel.

There are several other factors that are unique to the Santa Barbara Channel:

1. The long history of natural oil seepage in the area.
2. Unusually heavy winter runoff at the time of the spill which reduced salinities, increased sedimentation, and increased DDT in the channel.

Natural oil seeps have occurred in the Santa Barbara area throughout recent and geological history. During this period it is possible that the fauna in the area has developed some immunity to continuous exposure to low concentrations of oil. In the Coal Oil Point area where there is the largest concentration of oil seeps, there is no dearth of animals in the intertidal area. Divers have also observed *Diopatra* (Annelid), Nudibranchs, several species of fish, starfish, all living in areas of natural seepage.

The flow from these natural seeps is variable and activity may fluctuate rapidly during the day. After the heavy runoff in January, February there was an increase in natural seepage in the area. For example, tar mounds have been known to exist off Carpinteria Beach but no seepage had been observed in this area over recent years. Seeps were again active in this area over the March-June period of this year.

Unfortunately, little data is available on salinity changes caused by the heavy winter runoff. However, workers from Santa Barbara noted high mortality among sedentary intertidal species near the mouth of streams. Oil then came ashore and many hasty and untrained observers attributed

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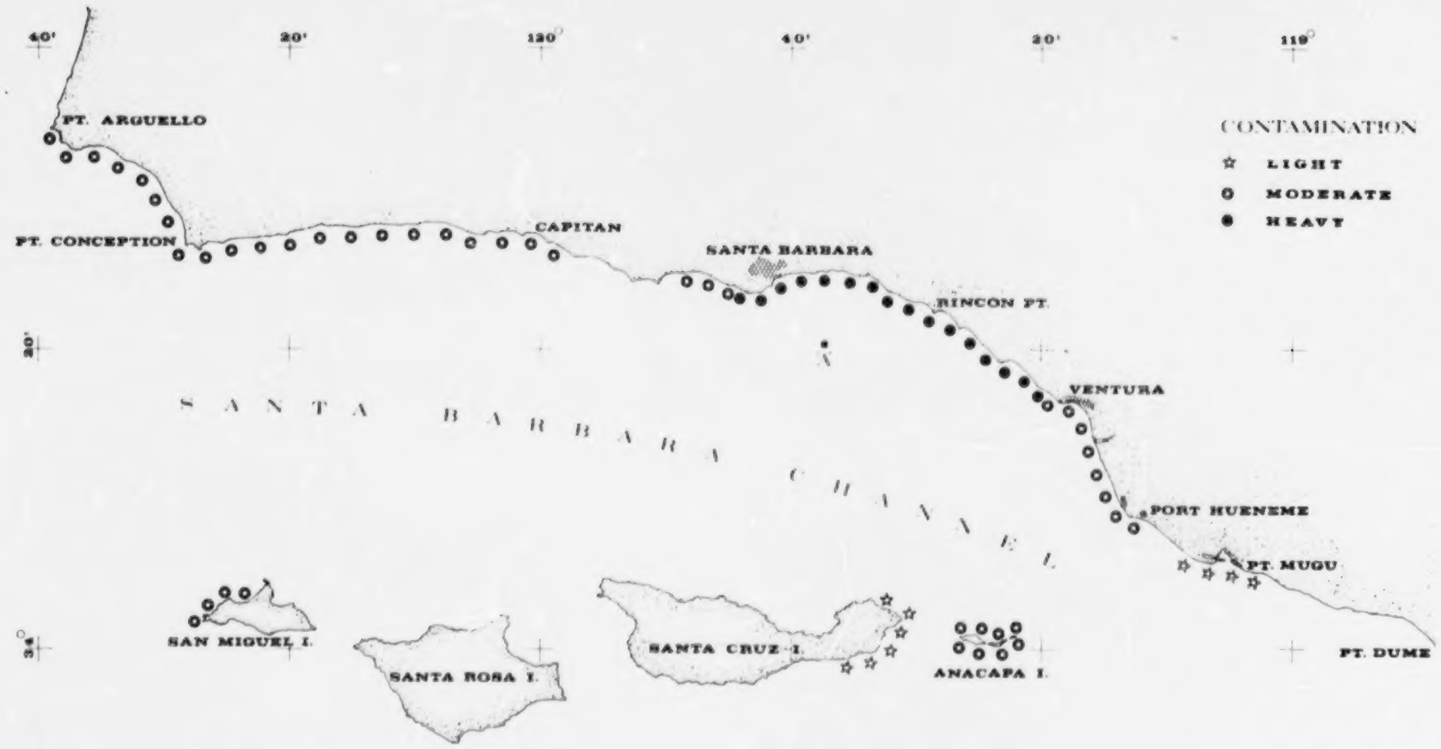

Figure 1. Area contaminated with oil from Platform A by March 30, 1969. (Data supplied by Coast Guard)

this mortality to the oil. Virtually no data is available on the change in pesticide levels in the Santa Barbara Channel. The rain occurred immediately after the citrus orchards were sprayed. As large quantities of oranges and other citrus debris were washed into the sea, most of these chemicals would have been washed seawards.

Soon after the spill both Federal and state authorities were active in the area. Several Federal authorities produced reports, which regretably, have not been released. U. S. Fish and Wildlife Service and California State Fish and Game have made cruises in the area. The former found that the plankton contained fish eggs and larvae of normal abundance and species. Phytoplankton counts were significantly lower than at a nearby station in January. The California State Fish and Game cruises recorded no significant changes in benthic and pelagic fish in the Santa Barbara Channel.

In mid February, the Western Oil and Gas Association granted the Allan Hancock Foundation $220,000 to study the biological and oceanographic effects of oil spillage in the Santa Barbara Channel following the 1969 blowout. At the time when the grant was received, all were optimistic that the flow of oil would be stopped and that over this period, we would obtain data on the recovery of the area.

The overall study can be divided up as follows:

1. Biology
   a. Phytoplankton productivity
   b. Zooplankton
   c. Benthic communities
   d. Intertidal and shallow water algal and invertebrate studies
2. Geology and Oceanography
   a. Planktonic, benthic and intertidal foraminifera
   b. Water Chemistry
   c. Geology and Oceanography
3. Bacteriology
   a. Effects of oil and benthic bacteria
   b. Effects of oil on sewage outfall

I shall only discuss the biological section of the program. Dr. Kolpack will discuss part of the geology and oceanography work. Briefly, the bacteriological work involves a study of changes in the bacterial population in areas of the oil spill and a study to determine if there are any changes in the bacterial population of sewage outflow in the presence of an oil slick. The oil slick cuts down the penetration of UV light and this could effect the bacterial population in the latter case.

Following the oil spill, the damage was most obvious in the intertidal zone and to the bird population. The Department of Fish and Game estimated the loss of birds due to the oil spill to be 3,600 by the end of March. This did not include birds which perished on the open water and failed to drift ashore. They also reported no influx or exodus of birds from the area but most birds appeared to avoid oil contaminated areas.

Concern was also expressed for the large marine mammals. The Grey Whales migrated north during this period and strandings were not higher than those reported in previous years. Autopsies on carcasses of stranded whales and seals failed to reveal the cause of death. Mortality data for the seal colony on San Miguel is not available for years prior to the oil spill. Hence, it is not possible to determine changes in mortalities in these colonies.

Intertidal rocky-shore transects were established at intervals along the southern California coast by Yale Dawson ten years ago. These were resurveyed by Mike Neushal and others from the University of California, Santa Barbara to determine the immediate effects of the oil spill on the intertidal areas. The work on the present grant overlaps with, and continues on from Neushals work. It is planned to continue these surveys after February 1970 to obtain long term recovery data. In general, where the oil has been lost from rocky substrates, recolonization has commenced.

The macrofauna on several sandy beaches are also being studied. The lack of background data, and the large seasonal and short term changes in the amount of sand on the beaches makes the effects of oil on sandy beach fauna difficult to assess. At present, there is a layer of oily sand on many beaches several feet below the surface. The macrofauna lives above this oily layer. With the onset of winter storms this oily layer will again be exposed and it will be interesting to see whether the animals avoid the oily sand or if the oil is now degraded to an extent so that it does not effect them.

The effects on the planktonic, benthic and pelagic species are less visible. The commercial fishing industry immediately started to report smaller fish catches. Fish catch data is being supplied by California Fish and Game while the Bureau of Commercial Fisheries is providing fish spotting data. Fish catch data is dependent on the willingness of fishermen to use their boats and equipment in oil water. Fish spotting data is considered to be 95% accurate. The oil in the Channel in February made it difficult to spot any fish; subsequent to this, the Pacific Mackerel (tons/flight) was more plentiful than in the previous two years while anchovys were more plentiful than in 1968 but available in similar quantities to 1967. Pacific Bonita which is normally absent in April, May and June, was not recorded from the Channel between February and July of 1969.

Benthic communities were intensively sampled in the Santa Barbara area between 1956 and 1959. This survey is providing background data for the present study. Samples are still being sorted and until this is complete, it is impossible to even guess at the causes of changes in the fauna. The zooplankton samples are also being analyzed. In this case, background data is available from these stations in the Santa Barbara Channel regularly sampled on CALCOFI cruises. There is no background data available for the phytoplankton productivity study. Indications to date suggest that phytoplankton productivity is not significantly effected by an oil slick.

The present study is still far from complete. As mentioned before, the emphasis is still on obtaining field data and, as a result, there is a lag in compiling results and drawing definite conclusions. The final report is planned for publication in September of 1970.

Some Ecological Effects Of Marine Oil Pollution

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Abstract

Oil at sea affects chiefly species associated with the surface; damage at sea by oil and dispersants after Torrey Canyon *were not as bad as expected.*

Slicks sometimes disappear naturally, how apart from physical actions may this be taking place? Bacteria can, under experimental conditions very favorable to their growth, assist in dispersal, sinking and decomposition of oil, and zooplankton can ingest oil droplets, but are these factors of significance at sea?

On shores after Torrey Canyon, *far more damage was done by excess detergent than by oil. Repopulation is following the expected sequence, most affected shores being still abnormal. Observations on oil left untreated in Cornwall, at Eleuthera and on the Devon coast show slow removal by various natural means, including the browsing action of fauna.*

Toxic detergents can affect the sublittoral zone, including species of economic importance. Areas liable to repeated pollution, such as estuaries and salt marshes, require special care. The use of newer dispersants of low toxicity is desirable here and on shores.

On The Open Sea

The organisms affected are those connected with the extreme sea surface. Birds show the most conspicuous and serious damage, and round the British coasts the slow-breeding awks are perhaps the worst hit; the subject is too complex to enlarge on here. It is well reviewed by Clark.[1]

Subsurface plankton collected after *Torrey Canyon* by the M.B.A. Ship showed damage to minute plant cells of the order Prasinophyceae which float at the surface. Eggs of pilchard also float; they showed a high proportion dead and there was a local shortage of pilchard larvae. This damage could have been from the toxic fractions of the crude oil or from the toxic solvent of the dispersants before they evaporated. Damage to mid-water forms was not detected after *Torrey Canyon*, nor even tainting of fish caught below a slick; in fact, at sea, effects of that major spill were not nearly as bad as expected. There seem to be misconceptions about this, probably due to press reports confusing damage by dispersants on shore and close in-shore with effects on open sea. A single catastrophic spill at sea is quite different from the often serious effects of chronic oil pollution in fairly enclosed waters.

At sea, slicks sometimes disappear naturally and one very much wants to understand the processes by which this can happen to assess how artificial aids, if and when applied, fit in with the natural processes. Obviously, physical factors, evaporation, spreading or alternative "mousse" (water-in-oil emulsion) formation and breaking up of slicks are of major importance. Photochemical oxidation is a possible means of actual decomposition of oil. Dr. ZoBell,[2] Gunkel and others have shown that bacteria, under certain conditions, can help in dispersal and sinking of oil, as well as in its decomposition. I too have recently made observations which confirm this under enriched conditions in the laboratory.

What happens on the under side of an oil slick at sea? Experiments with slicks on open water are essential because laboratory conditons are so different from those at sea. To what extent are separate droplets formed by natural processes? This is of major importance in connection with suggestions which have been made concerning the possible uptake of oil by zooplankton. I myself have seen that it is

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[1] Superior numbers refer to literature references at conclusion of text.

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possible for the large copepod, Calanus, to ingest oil droplets from artificial suspensions and this has been clearly demonstrated by Admiralty Materials Laboratory workers on some other zooplankton species (as yet unpublished). Any analysis of oil in zooplankton must clearly distinguish between mineral oils and biological oil reserves common in copepods, fish, etc. One must remember that copepods are by no means little automatic filtering machines; some, at least, are quite selective feeders and their appetites vary according to the time of year. Moreover, they undergo diurnal vertical migrations spending only part, if any, of their time very near the surface. Only just below the surface are the numbers of oil droplets likely to be perhaps of the same order of frequency as phytoplankton cells, but obviously both are very variable members.

Admiralty Materials Laboratory analyzed some samples of apparently clear water taken near slicks after *Torrey Canyon* and found in the surface samples 7-14 parts per thousand million of oil as compared with a "normal level" in English Channel waters of about 3 parts per thousand million. Oil was not detectable at subsurface depths (see Smith p. 34).[3]

The uptake of oil by zooplankton is being investigated in Britain because it could be the route by which oil products could enter the food chain. Copepods pass material through their guts rapidly; while some lighter fractions might diffuse through gut membranes, it seems very doubtful if mineral oils would be digested. Possibly oil droplets in faecal pellets might be in a more favorable position for bacterial attack while the pellets are sinking. During the diurnal migration of zooplankton, ingested oil could be carried down to deeper layers thus making a further small contribution to oil dispersal.

During weathering, the lighter fractions (some of which cause immediate acute toxic effects) have been evaporated or perhaps dissolved away. That weathered droplets seem to be fairly innocuous material, is suggested by the fact that thriving cultures of minute flagelles and ciliates (10-25 microns long) have often been found in my oily brews with numerous oil droplets (down to 1 micron diameter) in their food vacuoles, i.e., in very close contact with their protoplasm. This does not, however, mean that they are deriving nutriment directly from the oil but much more likely, they are feeding on associated bacteria, and they would later reject the oil as do many other larger animals. There could, however, be potentially toxic substances among the heavier ends as well, which could be accumulated via a food chain.

These observations are intended simply to show some of the ecological possibilities which have to be considered when discussing the fate of oil at sea. A great deal of further work is required on the many aspects of the subject.

On The Shore

First, one must distinguish between main types of beach pollutants. Chronic pollution, in which lumps of oil are stranded, has considerable nuisance value, but these lumps are of little consequence ecologically, so far as we have observed. Dennis[4], in his survey of the Atlantic coast of the States, deduced that coccina (small lumps of hardened oil often mixed with sand) must be abraided away by natural forces or they would accumulate more than they do. On the British coast, we have sufficient of this type of pollution on amenity beaches for some local authorities to think it worth while to collect and dump it. Dispersant treatment of this type of oil is a waste of time and money and could do considerable harm ecologically.

Catastrophic spills and lesser ones of fluid oil present altogether different problems. On amenity beaches it is acknowledged that they must be cleaned up because natural processes of removal are generally far too slow. We favor the use of mechanical means first, followed by the controlled use of dispersants where necessary, and would seek the use of the new types which have both low toxicity and reasonable efficiency.

On Sands

On the sandy parts of Cornish, shore oil soon became buried by wave-deposited clean sand and layers of oily sand underwent biodegradation with the production of grey sulphide layers; but, unless the oily sand layers were broken up, bacterial action was very slow. Treatment was mechanical and combined with the use of dispersant. Gunkel[5] recorded very high numbers of oil degrading bacteria on contaminated Cornish beaches. He also showed experimentally that the few bacteria which were able to survive the toxic dispersants, were then able to thrive on their kerosene extract solvents. A visual demonstration of this is seen in a jar containing 2 ml/litre of kerosene extract in nutrient sea water. Bacterial growth is obvious.

On the remote coral sand beach at Eleuthera (Bahamas), layers of buried oil from the General Colocotronis spill (March 1968) are seen. The beach was obviously very labile, so we thought that the porous sand particles would themselves act as dispersal agents for the oil and it was far better to leave such oil as had stranded to be dispersed and decomposed by natural agencies. Unfortunately, I have not been able to obtain any later reports on that beach.

Of oil spills on stable sands or muds on less exposed coasts, I have no personal experience. Such beach material contains a far richer fauna than does sand with low silt and organic content and it would seem all too likely that the infauna could be seriously affected by layers of oil.

On Rocky Shores

We have been collecting information on the biological changes and the fate of the oil itself, left untreated on rocky shores. Various physical factors are obviously very important: (1) the type and thickness of the oil, (2) the latitude, climate and time of year having their effects chiefly through viscosity differences, and (3) the exposure of the habitat to wave and sand abrasion.

The toxicity of the oil itself is sometimes considerable, sometimes not, according to its type and degree of weathering. There are various records of the toxic effects of fresh crude and of diesel oil. At the Tampico Maria spill, so well followed by North, Neushul and Clendenning[6], the heavy diesel oil was emulsified by the surf and had serious lethal effects on the fauna. Because it killed browsers, it encouraged subsequent algal growth. There is incidentally much in the general pattern of their observations on repopulation which we have also seen on Cornish rocky shores; but here the damage was done by the toxic detergents used in excess, the Kuwait crude oil itself, having been at sea for 10 days or so before stranding, had lost all the worst of its toxicity.

You may have heard of evidence that browsing fauna can play a part in cleaning off oil. On our temperate coasts, I consider it to be a small, but not insignificant activity of limpets, where, in the mid-tide zone, there has been a continuous cover of oil not so thick as to smother them completely. Cleared areas, tooth marks of oil and oily faeces show where they have been active and shell growth shows that the accidental uptake of oil has done them no harm–it is unlikely to have direct nutrient value. Patches of oil browsed away by limpets on a Brittany shore are seen in an area where no detergent was used but even after a year there was still much oil on the rocks. Spectacular removal of oil by chitons was seen at Eleuthera. Grey oily faeces of ground-up rock were common. (The animals have a continuous ribbon of teeth tipped with magnetite which enables them to erode the rock, in which process they obtain their normal food supply of algae which live within the porous surface.) About 50 per cent of the reef surface had been cleaned in about 15 days by chitons and nerites. Detergent treatment of oil on porous coral beach rock would have been most unwise, quite apart from killing off the useful fauna. Data recently published by Pearce and Ogren[7] on their observations on the San Juan spill (March 1968) and the conditions a year later indicate that where no cleaning was attempted there was little permanent damage except some areas of hard encrusted oil.

In October 1967, a spill of bunker oil landed as mousse only about 3 miles from the accident in Plymouth Sound, during a storm. We specially requested that some control areas be left untreated at Bovisand. The oil has been greatly reduced in thickness but even after 2 years the rocks at high tide level are still black with oil. At mid-tide level, browsing limpets and topshells have worked chiefly between the splodges of oil, leaving much of the oil untouched. A crust of fungal hyphae and algae seems to have protected the oil. This area lacked sand abrasion.

Effects Of Treatment By Toxic Detergents

Where detergents were used at Bovisand on rocks, much of it ran to waste because it does not readily penetrate "mousse." The ecological sequence so striking on the Cornish shores has been repeated here a year later. The changes extended well down the shore, below the oiled levels.

In Cornwall such was the zeal of the detergent cleaners (solvent emulsifiers) that very few oiled areas were left untouched. It must, however, be stressed that even in the affected 140 miles or so of Cornish coast, there were many undamaged sections from which recolonization took place. The most spectacular effect on these rocky shores was due to the killing of a high proportion of the browsing fauna, particularly limpets, which are both very vulnerable and also the most important herbivors of those shores. The removal of the grazers permitted the development of sporelings of algae. First there was a tremendously thick cover of green weed, chiefly *Enteromorpha* on the previously bare-looking rocks. The occasional surviving limpets were readily seen in bare areas a foot or so in diameter. By August young sporelings of brown fucoid algae were becoming numerous. They were better able to stand the exposed conditions. The brown weeds became so thick as to hinder the settlement of the usual fauna of mussels and barnacles for a time.

During the first winter the settlement of limpets began; this was of variable density on different shores. In some places they prevented any redevelopment of green weed, and usually there was no second settlement of fucoids. Where the limpets came back in force, they and the winkles made inroads on the fucoids, thinning out the small plants.

During the second summer and early autumn (1969), an abundant population of browsers had developed. Besides eating the fronds, radula marks could often be found on the stripes, thereby weakening the plant so that even if the stripe (or stalk) was not chewed right through, the frond could readily be torn away by wave action.

The rocks are now still heavily covered with seaweeds having a fauna under them more numerous and varied than before the detergent damage. It seems likely that in areas of moderate exposure, it will be several more years before anything like the original state is re-established. Places subjected to physical abrasion by shingle, etc., are passing through this ecological sequence more rapidly and already appear more or less back to normal, i.e., bare rock with fauna of limpets, winkles, barnacles and their predatory dogwhelks.

Such disturbances of shore habitats are certainly to be avoided in areas of special scientific interest, but detergent cleaning of rocks near amenity beaches can be accepted; providing it is done in limited amounts with careful washing away, preferably with sea water, there need really be very little damage. In the hands of workmen, dispersants of good efficiency and low toxicity are greatly to be preferred–such do exist now.

When man suddenly upsets nature on such a vast scale, complaints are rightly raised about it, especially when the long-term effects of the use of toxic material are unknown. The balance of shore life was upset and the rocks made dangerously slippery for several years, but it seems to me that though recovery is not yet complete, it is unlikely that any serious permanent damage will have occurred even after the colossal spillage experienced after the *Torrey Canyon* went aground. I would stress, however, that large amounts of oil could have been far more damaging in other areas. We hope that it was a once-only event to affect Cornish and Brittany shores, and that the drastic detergent treatment will never be repeated anywhere on such a scale. Because of the scale, the employment of inexperienced operators was unavoidable; and when one sees the difficulty of satisfactorily treating "mousse" with most dispersants, it is not in the least surprising that much of the older type toxic detergents ran to waste.

In Estuaries And On Salt Marshes

In areas liable to repeated spills, there is much greater need for care. At Milford Haven there are five recent oil refineries placed in an area of outstanding natural beauty. Oil spills are tackled at once on the water with dispersants and the area is remarkably clean for such a large oil port. Local hydrography with good flushing helps considerably. Occasionally, shores have to be cleaned but amounts of dispersant used are limited and carefully applied. Limpet kill has not been catastrophic, no phenomenal green phase has occurred, and the fauna has more or less recovered within a year. Nevertheless, there is anxiety about repeated oiling of the same area of rocky shores or salt marshes.

Very useful work is in progress by the Oil Pollution Research Unit based at the Orielton Field Studies Center on Milford Haven. Long-term effects of oil fractions and of oil spill removers are being investigated. Experiments similate field conditons by using short sharp sublethal doses of toxic detergents followed by recovery tests. There are oil-polluted experimental plots on the shore and marsh to provide controlled experiments and to follow up the effects of accidental spills. Accounts are available in the first annual report of the Field Studies Centre (Warden - E. B. Cowell)[8] and by A. Nelson Smith.[9]

On salt marshes, the once-only spill can have nasty effects but the seriousness to vegetation will depend on the time of year. Chronic pollution of marshes can certainly cause serious damage. When the grasses are destroyed, the habitat itself begins to erode away. Lesser damage may interfere with the area as a bird feeding-ground.

At present, dispersant application is strongly contra-indicated in estuaries or enclosed waters where there are shellfish of economic importance because of possible direct toxic effects and because of the increased risk of tainting from more widely-dispersed oil. Mussels can, however, readily pick up oil even without artificial dispersal. Much of it passed through the gut without harming them, but some may be left as a taint Man detects very low quantities of oil-tainted flavor in fish or shell fish and once a source of food has become suspect, the market is spoiled for a long time even though the damage may not be serious.

In The Sublittoral Zone

After the *Torrey Canyon* incident, we certainly did have local damage in the sublittoral zone, due to detergents running to waste, partly through lack of experienced operators. The effects on economic species, chiefly crabs and lobsters, were slight and temporary. The oil fortunately did not reach any of our oyster beds and even in Brittany by hard work and good fortune, the trouble was not as bad as expected. The incident has served as a very useful warning, alerting world attention to marine pollution problems as a whole.

Since food supplies from the sea will be in ever increasing demand, we must do all we can to minimize the damage from accidental or chronic oil pollution. This is an ecological effect of oil in a much wider sense.

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Microbial Modification Of Crude Oil In The Sea

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Abstract

Virtually all kinds of hydrocarbons and crude oils from many fields are susceptible to microbial oxidation. More than a hundred species of bacteria, yeasts, and fungi are able to oxidize hydrocarbons. Each species is limited in the kinds of hydrocarbons it can attack. Each species is also limited by the temperature, salinity, surface tension, pH, oxygen tension, and other environmental conditions at which it is biochemically active. Environmental conditions also affect the rate of microbial reporduction and oil oxidation. Enrichment cultures, consisting of several different species growing under optimal conditions, tend to convert crude oils and refinery products mainly to carbon dioxide and microbial biomass. From 10 to 90 per cent of the carbon may be converted into microbial biomass.

Oil-oxidizing bacteria are most abundant in coastal waters and mud where oil pollution is chronic. Such bacteria are extremely scarce in the open sea. In unpolluted waters the ratio of oil oxidizers to the total bacterial population in marine environments ranges from 1:100 to 1:10,000. In chronically oil-polluted coastal areas from 5 to 50 per cent of the bacteria may be able to oxidize one or more kinds of hydrocarbons. In such areas, bacteria in well-oxygenated waters might oxidize oil at rates ranging from 0.02 to 2 grams per square meter per day at 20° to 30°C.

Nearly all kinds of gaseous, liquid, and solid hydrocarbons in the paraffinic, oleofinic, and naphthenic series are susceptible to microbial oxidation. The microbial oxidation of hydrocarbons nearly always results in the formation of water, carbon dioxide, microbial cell substance or biomass, and a great variety of other end products, many of which have not been identified. More than a hundred species of bacteria, yeasts, and fungi have been found to oxidize one or more kinds of hydrocarbons. Such hydrocarbon oxidizers are widely distributed in oil-field soil, sump waters, and coastal areas, particularly in places subjected to frequent pollution by petroleum or refinery products. There are several reviews of the extensive literature on various aspects of the subject.[3, 7, 15, 22, 23, 48, 52, 71, 77, 78, 79]

Whether a given crude oil or product refined therefrom is attacked in marine environments depends upon several interrelated factors. Microorganisms capable of oxidizing hydrocarbons must be present and able to grow in the environment. Temperature, salinity, concentration of microbial nutrients, available oxygen, and the dispersion of oil in water are environmental conditions which govern the growth and physiological activities of microorganisms. Toxic pollutants such as hydrogen sulfide, cyanides from industrial wastes, certain heavy metals, free chlorine as in heavily chlorinated sewage, and phenols or cresols are examples of substances which may inhibit the growth of hydrocarbon oxidizers.

Occurrence of Oil Oxidizers in the Sea

Except in the immediate vicinity of land, neither oil-oxidizing yeasts nor mold fungi have been found in the sea. In order to place this generalization in proper perspective, though, it should be pointed out that relatively little effort has been devoted to looking for such microorganisms in the sea. Fewer than 5000 samples from the sea, which covers nearly 70 per cent of the earth's surface, is an average of only one sample per 28,000 square miles!

Oil-oxidizing bacteria appear to have a somewhat wider distribution in marine environments than yeasts or fungi, but such bacteria are only rarely found in the open ocean. Out of several hundred 10- to 50-ml samples of

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[3] Superior numbers refer to literature references at conclusion of text.

seawater collected beyond the continental shelf, fewer than 5 per cent have contained bacteria which could oxidize liquid hydrocarbons.

Tests for such bacteria consisted of treating 10- to 50-ml samples of recently collected seawater with medium- or light-weight paraffin oil along with enough ammonium nitrate and potassium phosphate to satisfy the nitrogen and phosphorus requirements of microorganisms. Either a millionfold or more increase in the microbial population or the modification of the mineral oil was accepted as evidence for the presence and activity of oil-oxidizing microorganisms. Microscopic observations were generally required to ascertain whether the microorganisms were bacteria, yeasts, or fungi. The minimum dilution or multiple tube technique,[2] with oil-enriched media, is commonly used to determine the most probable number (MPN) of oil-oxidizing bacteria in samples of soil, sediment, or water. For further details concerning analytical procedures, consult the literature.[29, 82]

Oil Oxidizers in Intertidal Areas. Wherever surveys have been conducted along the coast, oil-oxidizing microorganisms have been found in at least some of the 10- to 50-ml samples of seawater or bottom sediments collected between 40° S. Lat. and 60° N. Lat. I am aware of no surveys at higher latitudes. Most of the surveys have been made in the vicinity of coastal settlements or oil fields by people concerned with oil pollution or the microbial oxidation of oil. MPN values have been shown to range from < 0.1 to $> 10^8$ oil-oxidizing organisms per ml of marine mud or seawater.

One of the most extensive surveys was made along the coast of Louisiana by ZoBell and Prokop.[82] During a 3-year period they examined mud and water samples from more than 200 stations in the Barataria Bay region. Tests were positive in all 10-ml samples. In one series of 84 mud samples diluted to 10^{-6}, the MPN was $> 10^6$ in 8, $> 10^5$ in 11, $> 10^4$ in 25, and $> 10^3$ in 31 samples. In only 2 of the 84 samples were there fewer than 100 oil oxidizers per ml of mud. In another series of mud samples diluted to 10^{-9}, the MPN was between 10^8 and 10^9 per ml in several. The media were enriched with light-weight paraffin oil.

Employing identical methods, samples were assayed from 24 stations along the coast of Texas between Brownsville and Matagorda Bay. At 7 of these stations, negative results were obtained with 10-ml samples, meaning an MPN of < 0.1 per ml. At only 11 of the 24 stations was the MPN $> 10^4$ per ml.

Along the coast of southern California, the population of oil-oxidizing bacteria was found to range from nil in some 10-ml samples to $> 10^8$ per ml of mud. The largest populations occurred in San Pedro and Long Beach Harbors. Samples of beach sands and coastal seawater only rarely contained more than 10^4 oil-oxidizing organisms per ml, and often none could be demonstrated in 10-ml samples. From month to month at the same station, the population of oil oxidizers often changed by 4 or 5 orders of magnitude.

Oil-oxidizing bacteria, yeasts, and molds have been demonstrated in water and mud samples collected in harbors, bays, and estuaries in many parts of the world.

Biodegradability of Crude Oills

Crude oils from different fields and from different strata in the same field differ greatly in physical properties and chemical composition.[27] Along with hundreds of different kinds of hydrocarbons differing in their biodegradability and toxicity, most crude oils also contain small quantities of nitrogenous, oxygenated, and/or organic sulfur compounds. Such differences in composition help to account for the great differences observed in the vulnerability of various crude oils to microbial degradation. Observed differences in biodegradability are often also attributable to experimental or environmental conditions, especially the kinds of microorganisms which are involved.

I have never found a single microbial species which could noticeably degrade any crude oil, but most crude oils examined have been slowly degraded, oftentimes almost completely to carbon dioxide and microbial biomass, by *mixed cultures* consisting of numerous species. Most microbial species are highly selective in their ability to attack various constituents of petroleum and products formed therefrom.

In bringing about the complete degradation of crude oil, organisms which attack various hydrocarbon decomposition products, including complex organic acids, alcohols, ketones, etc., are as important as the organisms which breach hydrocarbons. In enrichment cultures, bacteria which utilize oil-oxidation products are generally more abundant than those which attack pure hydrocarbons. Attempts have not been made to identify all the microbial species involved in the degradation of crude oil by mixed cultures in seawater media, but from 20 to 30 different morphological and colonial types can usually be detected in most experiments.

Observations on Crude Oil. Circumstances attending the disappearance of crude oil spilled in soil, enclosed ponds, and other localized areas point to the involvement of oil-oxidizing bacteria. The gradual modification and disappearance of oils added to marine mud, pond waters, or moist soil, while oil persisted in similar sterilized mixtures, have demonstrated microbial degradation of oils from many fields.

More than 50 years ago, Sohngen[59] reported the oxidation of Russian and American crude oils by soil bacteria. As much as 750 mg of certain oils was oxidized per square meter per day at 28°C. During the last 50 years there have been numerous reports on the microbial degradation of various crude oils under both field and laboratory conditions.[15, 77, 82]

ZoBell and Prokop [82] examined crude oils from 58 oil fields in California, Louisiana, Oklahoma, Pennsylvania, and Texas for susceptibility to microbial degradation. Within 12 weeks at room temperature (21° to 28°C) every one of these crude oils (stripped of volatiles) was attacked by mixed enrichment cultures. This was indicated by either a. changes in the physical appearance of the oil, b. disappearance of the oil, c. weight loss of oil as compared with sterile controls, or d. oxygen uptake (BOD). When approximately 1 gram of volatile-free crude oil was added to 100 ml of aerated seawater enriched with potassium phosphate and ammonium nitrate, between 26 and 98 per cent of the oil was degraded by mixed cultures within 30 days at 25°C. Under similar conditions in sterile controls, there were from 0.3 to 6.7 per cent decreases in oil, attributable to autoxidation. Various fractions of certain crude oils resist bacterial degradation.[28]

After 9 weeks, 100-ml samples of most crude oils overlayering seawater in cylinders disappeared from sight, whereas most of the oil persisted in controls preserved with 0.6 per cent tricresol.[82] A little ether-soluble unsaponifiable residue was recovered from the bottom of cylinders in which the crude oil disappeared. It was not determined what percentage of the oily residue was extracted from oil-oxidizing bacteria which increased many millionfold in abundance during the course of the experiments. Certain bacteria, like many other kinds of living cells, contain from 0.1 to 2 per cent or more liquid and/or solid hydrocarbons, prominently normal paraffins.[7, 12, 15, 18, 24]

Toxic Substances in Crude Oils. High concentrations of a good many hydrocarbons and other components of petroleum may be bacteriostatic or bactericidal. Under ordinary environmental conditions, though, only a relatively few components of petroleum occur in sufficiently high concentrations to be injurious to microorganisms. Certain microorganisms may survive for weeks or months in crude oil or in reservoir fluids consisting of various proportions of oil and water.

In aqueous media as little as 0.01 per cent of such toxic substances as toluene, xylene, mesitylene, phenol, and cresol may inhibit the growth of certain sensitive microorganisms. On the other hand, other microorganisms may tolerate more than 0.5 per cent of these toxic substances. Bartels [5] described nine species of soil bacteria which could survive or grow in the presence of 0.38 per cent phenol. Among 96 other species of soil bacteria examined by Bartels, 46 could grow in the presence of 0.1 per cent phenol. Many microbial species have been examined which grew in the presence of 0.1 per cent of either phenol, cresol, toluene, naphthalene, paradichlorobenzene, or naphthol and used these compounds as the sole source of energy.[21]

Claus and Walker[13] investigated several strains of *Achromobacter* and *Pseudomonas* which grew with toluene, benzene, catechol, benzyl alcohol, or cresol as the sole source of carbon and energy. The oxidation products included acetic acid and pyruvic acid.

In most cases, when crude oils are mixed with seawater in proportions of one to fifty or more, not enough toxic components are dissolved in the aqueous phase to prevent microbial growth, although certain species may not grow or survive. Various microbial species differ greatly in their tolerance for toxic components in petroleum, and various crude oils differ greatly in their content of toxic substances.[28]

In assessing the ecological effects of oil in marine environments, much more information is needed on the toxicity of various petroleum components as well as the toxicity of oil-oxidation products for marine organisms, particularly the effects of such components or products on plant and animal life.

Biodegradability of Various Kinds of Hydrocarbons. Among the many factors which influence the biodegradability of hydrocarbons, molecular configuration seems to be the most important. In general, alkanes are attacked by more microbial species, more rapidly, and support more growth than either aromatic or naphthenic compounds. Within the alkane series, normal compounds are more susceptible to microbial oxidation than branched chain compounds. Biodegradability decreases as the number of branches increases and increases with the chain length of the branches.

Relatively few species oxidize methane, ethane, or propane, but some of those that do, do so quite rapidly under favorable conditions. Many more species have the ability to oxidize normal alkanes containing 10 to 18 carbon atoms than any other kind of hydrocarbons. With increasing chain length, alkanes seem to be increasingly more refractory to microbial oxidation, which may be attributable more to lower solubility in water than to lack of vulnerability to enzyme action. Waxes containing more than 30 carbons are quite rapidly oxidized by certain microorganisms when properly dispersed in aqueous media.

Certain microorganisms selectively attack unsaturated hydrocarbons, although many more species exhibit a preference for saturated compounds. The microbial oxidation of many different kinds of aromatic compounds has been investigated.[25, 26, 40, 52, 62, 66]

Introducing alkyl groups into the benzene ring tends to render the resulting compound more susceptible to microbial oxidation.[40] Toluene, $C_6H_5CH_3$, is generally more susceptible to bacterial oxidation than benzene, C_6H_6, xylene, $C_6H_4(CH_3)_2$, more than toluene, and mesitylene, $C_6H_3(CH_3)_3$, more than xylene. Soil bacteria which grew fairly well on butylbenzene, $C_6H_5C_4H_9$, failed to utilize either benzene or toluene.[25]

Although many exceptions have been noted, as a general rule, bacteria oxidize polycyclic hydrocarbons more readily than benzene.[78] Naphthalene generally promotes the growth of soil bacteria much more than benzene.[25, 26, 40, 63] Strawinski and Stone[62] found no bacteria in soil enrichment cultures which grew on benzene, but both biphenyl and naphthalene supported large bacterial populations. Tauson [65, 66] also found many soil bacteria which readily utilized biphenyl, naphthalene, anthracene, and phenanthrene. Such bacteria have also been found in the sea.[57] Gibson[25] has reviewed recent advances in the microbial degradation of benzene, anthracene, naphthalene, phenols, and other aromatic compounds.

A series of cycloparaffins from C_3- to C_8-membered rings were shown by Ooyama and Foster [47] to be oxidized by soil bacteria. The cycloparaffins were oxidized in part to the corresponding cyclomonoketones.

Non-Growth Hydrocarbons. The inability of a given microbial species to subsist on hydrocarbons is not proof of its inability to oxidize the hydrocarbons.[22] Probably widespread in nature are organisms which can oxidize certain hydrocarbons but cannot assimilate the primary oxidation products for either energy or cell building material. Enriching the hydrocarbon medium with minute amounts of certain sugars, simple organic acids, or peptones often enables bacteria to grow and to continue to oxidize non-growth hydrocarbons. Likewise, inoculating the hydrocarbon medium with other kinds of microorganisms which can assimilate the primary oxidation products often enables the first species to grow, perhaps at the expense of intermediate products of metabolism of the mixed microflora.

In many cases, mixed cultures have reproduced rapidly and degraded certain hydrocarbons almost quantitatively to carbon dioxide and microbial biomass, although single species isolated from the mixed cultures were unable to grow in mineral media containing only the hydrocarbons as a source of carbon and energy. Such circumstances serve to stress the ecological importance of studying the cumulative effects of mixed cultures on the degradation of crude oils under natural conditions of pollution. However, observations on pure cultures, cells harvested therefrom, or their enzymes acting on pure hydrocarbons are essential for an understanding of microbial metabolic pathways.

Oxygen Requirements for Oil Oxidation

The complete oxidation of 1 mg of hydrocarbon to CO_2 and H_2O requires between 3 and 4 mg oxygen, i.e., the BOD is 3 to 4. The theoretical BOD values for some representative hydrocarbons have been reported by ZoBell and Prokop,[82] who determined the actual BOD values for several crude oils and pure hydrocarbons.

At 20°C the 5-day BOD of 10 ml of various crude oil fractions per liter of seawater was found by Alyakrinskaya [1] to range from 2.46 to 5.40. With higher concentrations of crude oil, dissolved oxygen was depleted. With low concentrations of crude oil, the 5-day BOD at 20°C was between 42 and 64 per cent of the 20-day BOD.

Most hydrocarbon-oxidizing microorganisms require free or dissolved oxygen. When oil oxidizers are in contact with the normal atmosphere, as at the air-water interface, the supply of oxygen is usually adequate. In areas of intense microbial activity below the water surface, particularly in bottom sediments, oxygen may be a limiting factor. This depends upon how rapidly oxygen is consumed and how rapidly it is replenished. Replenishment may be by oxygen diffusion, water turbulence, or photosynthetic activity in shallow water.

Depending largely upon temperature and salinity, the dissolved oxygen content of seawater in equilibrium with the normal atmosphere is between 6 and 11 mg per liter. This much oxygen is required for the complete degradation of from 2 to 4 mg of crude oil. Taking 3 as its mean BOD value, it would require all of the dissolved oxygen in about 320,000 gallons of seawater for the complete oxidation of 1 gallon of crude oil. The complete oxidation of one barrel of such crude oil would require all of the dissolved oxygen in about 40 acre-feet of seawater, assuming no replenishment from the atmosphere or photosynthetic activity.

Provided some free oxygen is available, the oxygen tension does not seem to be a limiting factor until the partial pressure of oxygen becomes so low that oxygen is consumed more rapidly than it can be replenished by diffusion or otherwise.

Other Hydrogen Acceptors. Under certain conditions, a few microbial species are able to attack hydrocarbons in the absence of free oxygen. In laboratory experiments, nitrate has been shown to serve as a hydrogen acceptor for certain hydrocarbon-oxidizing bacteria.[10, 64, 81] A strain of *Pseudomonas aeruginosa* utilized *n*-octane and *n*-hexadecane anaerobically while reducing nitrate to nitrite.[69] Theoretically around 4 mg of nitrate is required for the complete oxidation of 1 mg of mineral oil.

Based on observations with washed cells of *Pseudomonas stutzeri* in manometric apparatus, Hansen and Kallio [30] concluded that pure cultures cannot utilize nitrate as the terminal oxidant for hydrocarbons. They pointed out, though, that "once the hydrocarbon structure has been breached by the introduction of oxygen, by means of peroxidation or oxygenase action, oxidation at the expense of nitrate reduction and, presumably, sulfate reduction occurs readily."

Under natural conditions, it may matter little whether nitrate can provide oxygen for the microbial oxidation of oil in anaerobic environments, because nitrate is generally absent. However, from an ecological, industrial, or engineering point of view, it may be of importance to know whether treating oil-polluted waters or oil-fermentation tanks with nitrate promotes the oxidation of oil.

The utilization of hydrocarbons by strictly anaerobic sulfate-reducing bacteria has been reported by several investigators.[16, 17, 19, 31, 38, 46, 54, 68, 69, 82] In 78 out of 100 mud samples from Barataria Bay, 1-gram inocula were found by ZoBell and Prokop [82] to decompose mineral oil under strictly anaerobic conditions and to reduce sulfate. Similar observations were made by Ivanov,[31] who demonstrated that mixed cultures from various sources reduced sulfate in mineral media with crude oil as the only source of organic matter. His observations, however, failed to prove whether pure cultures of sulfate-reducing bacteria can oxidize petroleum hydrocarbons.

The majority of 38 cultures of sulfate-reducing bacteria isolated from oil fields were found by Dostalek *et al.* [16] to assimilate paraffinic hydrocarbons. Some of these cultures (probably mixed) reduced the relative viscosity of certain mineral oils from 115.3 to 112. About half of the 47 cultures of sulfate-reducing bacteria examined by Updegraff and Wren [74] reduced sulfate in mineral media enriched with a mixture of hexadecane and crude oil.

It seems doubtful whether pure cultures of sulfate-reducing bacteria assimilate highly purified hydrocarbons in mineral media containing no other source or organic carbon. There is overwhelming evidence, though, that certain mixed cultures slowly oxidize hydrocarbons while reducing sulfate. The reaction is accelerated by traces of organic nutrients in concentrations much too low to account for the quantities of sulfate reduced.

Dispersion of Oil in Water

Under otherwise comparable and optimal cultural conditions, the rate at which most liquid and solid hydrocarbons are oxidized is limited by their solubility or dispersion in aqueous media. The concentration of gaseous hydrocarbons in aqueous media is largely a function of the partial pressure of each. Owing to the low partial pressure in open systems, rarely is as much as 10 ppm of any gaseous hydrocarbon found in the sea. The solubility of only a few liquid hydrocarbons is more than 10 ppm in water at temperatures extant in the sea (mostly -2° to 30°C). The vast majority of liquid and solid hydrocarbons are less soluble than 1 ppm.

Aqueous emulsions, dispersing agents, and adsorption of hydrocarbons on solid surfaces help to render them susceptible to the action of enzymes. Prerequisite to microbial oxidation, properly oriented molecules must come into contact with specific catalyzing enzymes and active oxygen. There are many ways in which natural and/or experimental conditions help to satisfy this prerequisite.

Ways in Which Oil May Be Dispersed. Providing relatively large air-surface areas helps to place more oil in contact with aqueous media and with atmospheric oxygen. In nature, the sea provides the largest surface area over which certain oils may spread to almost monomolecular thinness. A gallon of spreading oil could cover many acres.

Sharp shaking or sparging oil and water mixtures with air tends to disperse both oil and oxygen throughout the medium.

Certain chemical emulsifying or oil-dispersing agents often help to make oil more available to microorganisms by increasing the contact of hydrocarbon molecules with microbial enzymes and oxygen. But, in experimental work in the laboratory as well as in field applications, all due precautions must be taken to avoid adding such chemical agents in deleterious concentrations, because: (a) Many detergents and emulsifying agents are bacteriostatic in concentrations no higher than a few parts per million, (b) Certain oil-dispersing agents may provide preferred sources of carbon for bacteria, thereby diminishing the oxidation of hydrocarbons or making it difficult in laboratory experiments to tell whether bacterial growth or oxygen uptake is attributable to hydrocarbon or additive oxidation, (c) High concentrations of detergents or other oil-dispersing agents may be injurious to plant and animal life in the sea. The excessive use of detergents off the coast of West Cornwall, following the wreck of the tanker *Torrey Canyon* in 1967 when about 120,000 tons of Kuwait crude oil was spilled in the sea, probably damaged marine life much more than the oil.[8, 14, 34, 45, 58, 76]

Absorbing oil on solids such as sand grains, ground glass, glass wool, asbestos fibers, chalk, gypsum, and other chemically inert particles often promotes the oxidation of oil by virtue of the increased surface exposed to microbial enzymes. Probably such adsorption of oil on particles also results in more favorable orientation of hydrocarbon molecules.[77, 80] Dispersing oil in solidified mixtures of calcium carbonate and calcium sulfate (Plaster of Paris) renders it much more susceptible to microbial oxidation.[67, 77] In order to help counteract the adverse effects of oil from the *Torrey Canyon* along the North Brittany coast, the French used about 3000 tons of chalk (largely calcium carbonate) treated with sodium stearate. The latter is an effective emulsifying agent. The mixture of chalk and sodium stearate, called "craie de Champagne," is believed to have made the oil more available to microorganisms.

The French workers believed, but failed to prove, that the phagotrophic flagellate, *Noctiluca miliaris*, ingested the oil-soaked "craie de Champagne" along with large numbers of attached bacteria. Such particles are known to be ingested by numerous species of protozoans and by myriads of other socalled mud-eaters or filter-feeders which are generally abundant in coastal waters and on the sea floor. Except under the most extreme conditions, there is no evidence that such animals are injured by oil pollution. Certain animals digest oil, although it has yet to be determined the extent to which intestinal bacteria contribute to the oxidation of ingested hydrocarbons. Unquestionably, the bacteria which animals ingest contribute substantially to the nutrition of many species.

Heating aqueous mixtures of oil generally increases the dispersion of liquid and solid hydrocarbons. Such dispersion, however, may be reversible and, moreover, there are practical limits in the laboratory as well as in the sea to which aqueous mixtures of oil can be heated.

Effect of Temperature

More important than its effect on the solubility or dispersion of oil in water is the effect of temperature on the rate of microbial growth and activity. To set the stage for this discussion, it should be pointed out that the temperature range of more than 99 per cent of the marine environment by volume or area is -2° to 30°C. This is the range within which most species of marine microorganisms grow best, although microbial growth has been observed in the laboratory at temperatures as low as -7.5°C and as high as 95°C at normal pressures.

The microbial decomposition of hydrocarbons has been demonstrated at temperatures as low as 5°C and as high as 70°C. Klug and Markovetz [33] observed the growth of bacteria on *n*-tetradecane at 45° to 70°C. Enrichment cultures of a thermophilic *Bacillus* utilized normal C_{12}-C_{20} alkanes at temperatures ranging from 37° to 70°C.[39] Most observations have been made at temperatures between 20° and 37°C. Studies on microbial dissimilation of other carbon compounds at low temperatures suggest that certain species may be able to oxidize hydrocarbons at temperatures at least as low as -2°C, the freezing point of high salinity seawater.

Species, salinity, pH, nutrients, and pressure are some of the factors which influence microbial reproduction rates at different temperatures. Under non-stress conditions at temperatures below their optima, the generation time of most bacteria increases from two- to threefold for each 10°C decrease in temperature. Thus a given species, which reproduces most rapidly at 25°C, may reproduce only one-half to one-third as rapidly at 15°C, and only one-half to one-third as rapidly at 5° as at 15°C. This means that, when growth is at the expense of oil, theoretically this species could be expected to oxidize the oil only 1/9 to 1/4 as rapidly at 5° as at 25°C. The few species which have been tested oxidized hydrocarbons from 10 to 20 times more rapidly at 25° than at 5°C. A culture studied by Sohngen [59] was found to oxidize as much paraffin wax in two days at 28°C as in a week at 20°C. Similarly, Stone *et al.* [61] found hydrocarbon oxidizers to be much more active at 30° than at 20 °C.

Microbial Activity at Low Temperatures. It is not known whether psychrophilic oil oxidizers exist or whether such microorganisms could be "trained" to oxidize oil rapidly at refrigeration temperatures, say -2° to 5°C. Other kinds of cold-loving bacteria which grow best in cool (< 15° to 20°C) media or environments, abound in certain refrigerated foods,[20] in Antarctic waters,[49] and in the deep sea where the temperature is nearly always lower than 5°C.[83, 84] The basic nature of marine psychrophilic bacteria has been reviewed by Morita.[43]

The obligate marine psychrophile, *Vibrio marinus,* reproduces rapidly and oxidized glucose at 4°C and also at 15°C.[43] Its maximum temperature is around 20°C. Its generation time was 80 minutes at 15°C and 226 minutes at 3°C.[44]

The generation time of microorganisms at various temperatures is influenced by other environmental conditions and especially by the nutrient composition of the medium.

Nitrogen and Phosphorus as Nutrients

Besides energy sources, oil oxidizers, like all other kinds of microorganisms, require utilizable sources of C, Ca, Mg, K, S, Fe, N, and P, plus various trace elements. With the exception of utilizable organic carbon, nitrogen, and phosphorus, all of the elements in utilizable forms are usually in adequate supply in soil and seawater. A lack of utilizable compounds of nitrogen and sometimes phosphorus may limit the growth of oil-oxidizing microorganisms in seawater.[32, 35]

In laboratory experiments, it is nearly always necessary to enrich seawater with compounds of nitrogen and phosphorus to provide for the maximum growth of oil oxidizers. The nitrogen and phosphorus requirements of most oil oxidizers are satisfied by the addition of several parts per million of ammonium phosphate. Equivalent quantities of other salts such as ammonium sulfate, ammonium chloride, ammonium nitrate, potassium phosphate, sodium phosphate, or calcium phosphate, for example, serve just as well and may have certain biological or economic advantages.

Laboratory experiments suggest that a lack of available nitrogen and possibly phosphate might be a limiting factor for the growth and activity of oil-oxidizing microorganisms in certain marine environments. For optimal operation of biofilters designed to free waste waters of hydrocarbons, it is sometimes necessary to enrich the waste waters with appropriate sources of nitrogen and phosphorus. A good many other compounds besides ammonium salts may satisfy the nitrogen requirements of certain microorganisms. Nitrates may be assimilated by some oil oxidizers. The rapid disappearance of oil from coastal areas occurred when appropriate sources of nitrogen and phosphorus were provided.[35]

Products of Oxidation

An expansive array of organic acids, lipids, esters, complex alcohols, ketones, aldehydes, polysaccharides, microbial proteins, and other substances have been shown to result from the microbial oxidation of petroleum hydrocarbons.[6, 7, 15, 23, 36, 41, 51, 53, 60, 71, 72] Figuratively, however, the surface has barely been scratched in determining what products might result from the oxidation of the thousands of different kinds of hydrocarbons by the dozens of microbial species under various experimental, industrial, or natural environmental conditions.

An important and almost totally unexplored facet of the oil pollution problem is the effects of oil-oxidation products on marine plants and animals. Microbial proteins and other cell substances synthesized by oil-oxidizing microorganisms are probably beneficial to phagotrophic animals.

Microbial Biomass. Meriting special mention is the microbial biomass resulting from the growth of oil-oxidizing microorganisms. From about 10 to more than 90 per cent of the carbon content of hydrocarbons undergoing microbial oxidation may be converted into microbial cell substance or biomass consisting mainly of proteins, nucleic acids, lipids, and polysaccharides. In marine environments such microbial biomass may contribute substantially to the nutrition of marine animals. The microbial conversion of hydrocarbons into proteins has become an industrially interesting reaction.[11, 15, 55]

A species of yeast belonging to the genus *Candida* was found to convert up to 82 per cent of *n*-octadecane into yeast biomass.[50] Soil *Candida* species studied by Miller and Johnson [42] converted from 71 to 94 per cent of normal C_{12}-C_{18} paraffinic hydrocarbons into yeast biomass, about half of which was protein. These are exceptionally high yields. Yields from mixed cultures after prolonged incubation are often less than 10 per cent. The average yield for numerous pure and mixed cultures of bacteria, yeasts, and molds under various conditions of cultivation fall between 30 and 40 per cent, about half of which is protein.

Oil Oxidation Rates

The rate at which oil undergoes microbial oxidation is influenced by the abundance and kinds of microorganisms, the dispersion of hydrocarbons in the medium, oxygen supply, temperature, the chemical composition of the oil, and several other factors. Above the level of its solubility in water, the amount of oil added to seawater may be detrimental.

Excessive quantities of crude oil or tarry substances may retard microbial oxidation rates for various reasons: (a) Thick layers of oil on the surface of water may diminish the uptake of oxygen from the atmosphere or diminish the penetration of sunlight essential for the photosynthetic liberation of oxygen, (b) Hydrocarbons within multimolecular layers of oil, greases, or tars may be almost completely out of contact with microbial enzymes, water, or free oxygen, and (c) The concentration of water-soluble toxic substances can be expected to increase as the quantity of oil increases in a given area.

Within the range of 0.5 to 50 ml of crude oil per liter of seawater, the 5-day BOD at 20°C was found[1] to increase only 2 to 4 times when the amount of oil was increased 40 to 100 times. Above 50 ml per liter, adding more oil had little effect on its rate of oxidation. In these BOD experiments, various crude oils were oxidized at rates ranging from 0.2 to 2 mg per liter per day at 20°C.

When dispersed on glass wool, paraffin wax was oxidized by marine bacteria in BOD bottles at rates ranging from 0.4 to 1.4 mg per liter per day at 20° C.[77] Believing that contact of oil with culture medium was rate limiting, Tauson and Shapiro[68] expressed the rate of oil oxidation in terms of surface area of water overlayered with oil. Crude oils were oxidized at rates ranging from 0.5 to 1.3 grams per square meter per day at 25°C. There are numerous reports on the microbial oxidation of crude oils, lubricating oils, cutting oils, and oily wastes at rates ranging from 0.02 to 2 grams per square meter per day at 24° to 30°C.[3, 4, 9, 15, 32, 37, 56, 75, 82]

Almost completely lacking are meaningful data on the rate of oil oxidation at temperatures in the psychrophilic range, say -2° to 14°C.

Summary and Conclusions

Under favorable environmental conditions, most kinds of petroleum hydrocarbons and associated products appear to be susceptible to oxidation by various kinds of bacteria, yeasts, and fungi. Such oil-oxidizing microorganisms are often abundant in soil, marine sediment, and seawater in coastal areas where natural or man-induced oil pollution is chronic. Such microorganisms are extremely sparse or absent in the open ocean. Nothing is known about the occurrence or activity of oil-oxidizing microbes in marine environments north of the Arctic Circle or in Antarctic areas.

Mixed enrichment cultures generally degrade crude oils more rapidly and more completely than pure cultures of microorganisms. Degradation products include a great diversity or organic acids, complex alcohols, aldehydes, ketones, microbial proteins, and other substances. It has yet to be determined whether any of the degradation products are produced in sufficient concentrations in marine environments to be injurious to plant or animal life. Depending upon (a) the microbial species present, (b) the composition of the oil, and (c) environmental conditions, from 10 to 90 percent (mean value around 35 per cent) of the carbon content may be converted into protein-rich microbial biomass. Such biomass may provide nutriment for protozoans and other phagotrophic animals.

Microbial degradation seems to be Nature's way of cleaning up chronic oil pollution of surface soil, beaches, and coastal waters. Microbial degradation is most efficient in removing relatively low concentrations of oil. Thin films of oil on the surface of water or on solid surfaces are most vulnerable to microbial attack. Though not effective for the rapid removal of massive volumes, microbial degradation is probably very important in ameliorating and curtailing damage from oil spills. It might be possible to accelerate the microbial process and to increase its effectiveness by treating oil polluted areas with enrichment cultures which have been "trained" to attack the various kinds of hydrocarbons most likely to be present in the area. Seeding oil-polluted areas with enrichment cultures offers promise.

Post-Conference Summary

Most of the generalizations summarized in this paper are based on observations made under carefully controlled experimental conditions designed to simulate the marine environment. All possible precautions should be exercised in extrapolating the results of such experimental work to the assessment of what actually happens in oil polluted areas. It may be nonsense to talk about microbial reaction rates and oil-degradation products in oil-polluted areas unless all cogent conditions in the field and laboratory are comparable. Among the most important conditions which influence the microbial degradation of oil in the sea are the following. (a) abundance and kinds of microorganisms present, (b) concentration of microbial nutrients, especially utilizable nitrogen and phosphorus compounds, (c) oxygen supply, (d) chemical composition of the oil, (e) temperature, and (f) dispersion of oil in water.

Although dispersing oil in water generally promotes its degradation by microorganisms, certain chemical dispersants may inhibit microbial activity in various ways. Certain dispersants are toxic because they damage cell-membrane permeability or because they irreversibly denature essential enzymes. Certain dispersants inhibit microbial activity by reducing the surface tension of aqueous media to unfavorable levels. For most bacteria the lethal level is between 25 and 35 dynes/cm. Surface tensions lower than 45 dynes/cm are often inhibitory. Oil-oxidizing microorganisms are generally most active in aqueous media having a surface tension between 45 and 60 dynes/cm. This is considerably less than the surface tension of normal seawater (73 to 74 dynes/cm at 20°C). Thus a little surface-tension depressant may promote the microbial degradation of oil, but too much may have a retarding or lethal effect.

Foremost among the many unsolved problems confronting environmental engineers concerned with oil pollution are the following: (a) the compatibility of various chemical dispersants with microorganisms, (b) the effects of oil-oxidation products on the well-being of plant and animal life, (c) the rate and extent of oil oxidation at temperatures in the range of -2° to 15°C, (d) data on the abundance and kinds or varieties of oil-oxidizing microorganisms in areas subject to oil pollution both before and after the area has become polluted, and (e) observations on the concentration of dissolved oxygen and microbial nutrients in oil-polluted areas to ascertain whether either becomes a limiting factor for oil oxidation.

Owing to the time required for the microbial degradation of oil, the microbial method cannot be recommended as a means for quickly cleaning up massive oil spills. Microbial degradation seems to be most effective for removing films or minute droplets of oil from water, beaches, shellfish beds, and other submerged surfaces.

This seems to be Mother Nature's way of cleaning up oil pollution in soil and sea. Man must cooperate with Nature by not overloading the ecosystem and by not upsetting the biological balance. When oil is spilled, I recommend the quick removal of as much oil as possible after which seeding with appropriate mixed cultures might be indicated depending upon the circumstances. The use of non-toxic dispersants or other emulsifying agents may accelerate the microbial degradation of oil.

During the final discussion period on December 17, there was a question from the floor concerning fungi as oil oxidizers. Numerous kinds of fungi, yeasts, and closely related actinomycetes have been shown to degrade a wide variety of crude oils and derivatives therefrom ranging from kerosene and jet fuel to paraffin wax.[77] Species of *Aspergillus, Botrytis, Candida, Cladosporium, Debaromyces, Endomyces, Fusarium, Hansenula, Monilia, Penicillium, Actinomyces, Micromonospora, Nocardia, Proactinomyces*, and *Streptomyces*, which oxidize a great variety of hydrocarbons are widely distributed in soil, freshwater, and coastal waters. From 178 water samples associated with jet fuels Churchill and Leathen (U.S. Air Force, A.S.D. Tech. Rept., 61-193, pp. 1-66, 1961) isolated 75 fungal types and 104 bacterial types. According to Davis,[15] organic material of "paraffin dirt" is heavily impregnated with fungi, yeasts, actinomycetes, and bacteria.

The question from the floor concerning the biodegradability of carcinogenic hydrocarbons was answered in part by citing a paper by Sisler and ZoBell entitled "Microbial Utilization of Carcinogenic Hydrocarbons" (*Science*, vol. 106, p. 521, 1947). Phenanthrene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, and several other polycyclic hydrocarbons were shown to be from 11 to 68 per cent oxidized to carbon dioxide by mixed cultures of bacteria within four days at 32°C. The microbial metabolism of polycyclic hydrocarbons is treated in much greater detail in books by Beerstecher[7] and Davis.[15]

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Microbial Degradation Of Normal Paraffin Hydrocarbons In Crude Oil

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Abstract

Experiments designed to measure the oxidation and degradation of crude oils by naturally occurring marine microorganisms are presently being conducted. Fifty active microorganisms have been isolated in enriched oil degrading cultures have been isolated in enriched seawater containing crude oil. Oil degradation has been determined with gas chromatography, wet combustion, and by measurement of surface tension. Normal paraffin hydrocarbons through C-26 are degraded by two different groups of microorganisms–those growing in the oil phase only and those growing in the aqueous phase. Emulsification of the crude oil through production of surfactants was observed in many of the enriched cultures. Microbial degradation of 35 to 55 per cent of oxidizable crude oil occurred within 60 hours.

It is generally known, supported by the lack of recent petroleum deposits, that indigenous microbial populations must eventually degrade in our geological time most of the hydrocarbons which are released into the marine environment.[1] Removal of hydrocarbons from the sea surface by microorganisms can be effectively significant through two functional aspects–direct oxidation for carbon and energy to CO_2 or intermediate products,[2,3,4] or by production of surfactants which may emulsify more recent oil materials.[5]

Because of the significance of oil pollution today, it is necessary to understand the above microbial processes with the thought of increasing microbial oil degradation by seeding an area where oil has been introduced. Thus, it may be possible that large quantities of selected microorganisms, offered growth enhancing properties, could hasten degradation and ultimate removal of pollutant hydrocarbons.

We have recently begun a study, sponsored by the FWPCA, to determine the feasibility of such a seeding operation to aid in oil spill cleanup operations in the marine environment.

Methods

Initial experiments, in addition to determining nutrient requirements and isolation procedures, were designed to measure microbial produced changes in oil at water interfaces and in straight chain hydrocarbons in crude oil. For isolation of cultures, soil and water continuously exposed to hydrocarbons for several years were sampled. Oil oxidizing organisms, to be described later, were isolated off the California coast (C-63), from Boston Harbor (BHMO), from a refinery drainage ditch in Pennsylvania (SOCLA), near an oil rig in the Gulf of Mexico (OILRIG), in the ship channel at the Florida State University Marine Laboratory on the Gulf of Mexico (TPLA), and in a thick oil film on the Mississippi River near New Orleans (NOLA). For experimental purposes, a light southwest Louisiana crude and an asphaltic California crude (E-76) have been used as reference hydrocarbons.

Oil active microorganisms were isolated from oil contaminated seawater and sediments by techniques based on work by Bushnell and Haas (1941) and Davis (1967). The following scheme has been followed.

Approximately 1.0 ml liquid or a 0.1 gm soil sample was added to a 50 ml Erlenmeyer flask containing 20 ml enriched seawater of the following composition: 1 PPT $(NH_4)2\ SO_4$, 10 PPM K_2HPO_4, 5 PPM yeast extract, and 10 PPM EDTA, adjusted so the final PH after sterilization was 8.1. The mixture was overlain with 5 drops of 0.45 micron membrane filtered crude oil, vigorously rotated for

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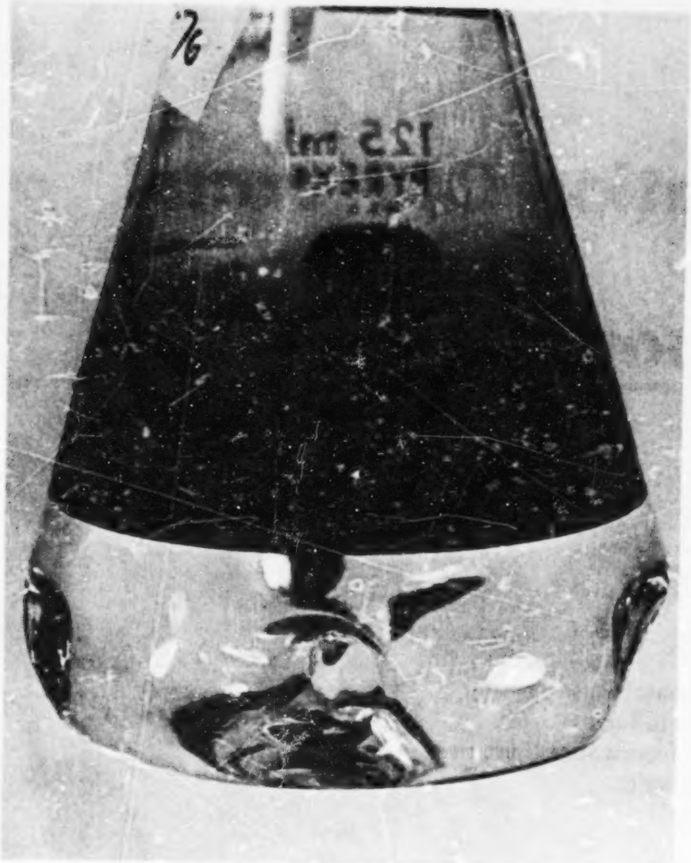

Figure 1. Control sample of a California crude.

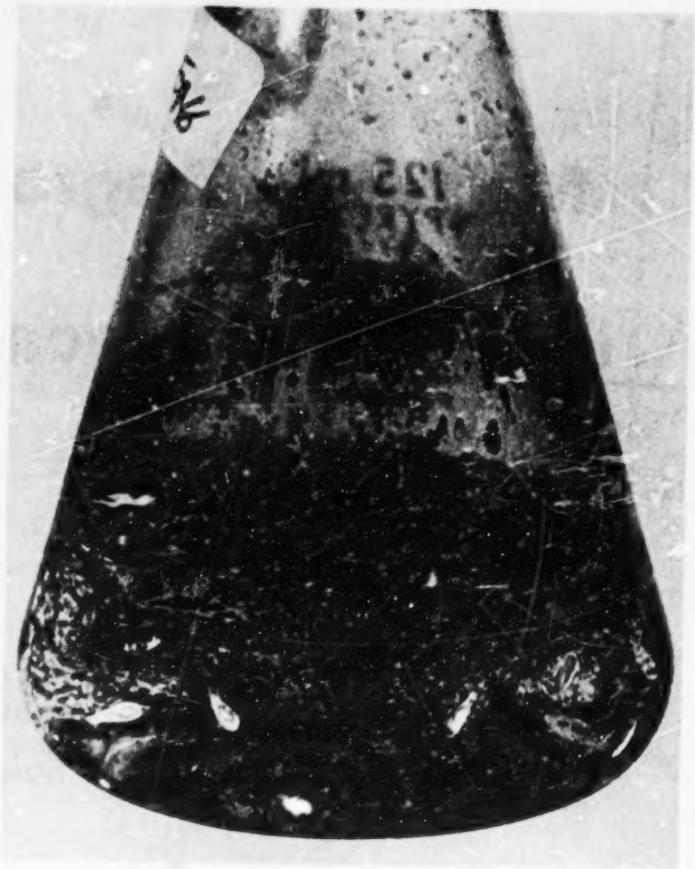

Figure 2. Sample shown in Figure 1 after 72 hours growth of an oil positive culture.

48 hours at 32°C, then scored positive or negative based on cell density and oil emulsifying ability. A loopfull of the most active cultures was then transferred twice on the same medium with 48 hour incubation periods and thereafter maintained on an enriched seawater agar + oil slant.

Experiments were conducted following the classical bacteriological technique of streaking the cultures out on a seawater agar + oil plate, picking colonies, then maintaining and working with pure cultures. However, the various pure cultures, even when recombined, invariably resulted in the loss of hydrocarbon degrading ability as compared to the original mixed culture. Others[4] have also used mixed populations to study microbial degradation of crude oils. Our mixed cultures maintain themselves well on slants, and approximately 50 cultures are presently being examined.

The cultures are designated by origin of sampling and have not yet been characterized for individual strains of microorganisms. Of our fifty cultures in stock, results of crude oil degradation by six of our most active mixed cultures previously referred to by sample location, will be reported here.

Several methods have been devised to quantify rates of oil degradation by microorganisms. B.O.D. has been used to calculate rates of hydrocarbon consumption under ideal conditions,[7] as has weighing the residual crude after extraction.[4] Other methods include combustion and carbon balance.

Each of these techniques has its limitations. For our work we chose the following scheme which we felt would give us the most information to use in selecting appropriate cultures as seed organisms.

1. Growth in enriched seawater
2. Observation of the aqueous and oil phases
3. Surface tension
4. Benzene extraction and Gas Chromatography
5. Wet Combustion

To attain maximal growth one loopfull of a 48 hour liquid culture was inoculated into 50 ml of enriched seawater overlain with 0.1 per cent sterile crude oil. The culture was incubated at 32°C on a rotary shaker. This seawater to oil ratio limits maximal hydrocarbon degradation as cell densities of 10^9 cells/ml and pH changes from 8.1 to 5.6 were produced after 36 hours. Further activity was apparently severely limited under these crowded conditions and pH change. We have since shown that increasing the seawater to oil ratio permits more complete oxidation of the crude oil. A "chemostat" type of apparatus is presently being tested that may alleviate the problems inherent in a closed system.

After a period of growth visual changes in the aqueous phase (such as cell density, color, pH), as well as changes in the oil film (emulsification and inability to coat the container walls) were used to identify microbial activity.

Two distinct types of cultures active on the crude oils have been isolated—microorganisms that grow in the oil phase only (these will be referred to as oil positive), and those that grow in the aqueous phase. Figure 1. shows the control sample of a California crude (E-76). There is a distinct surface film and the oil clings to the side of the

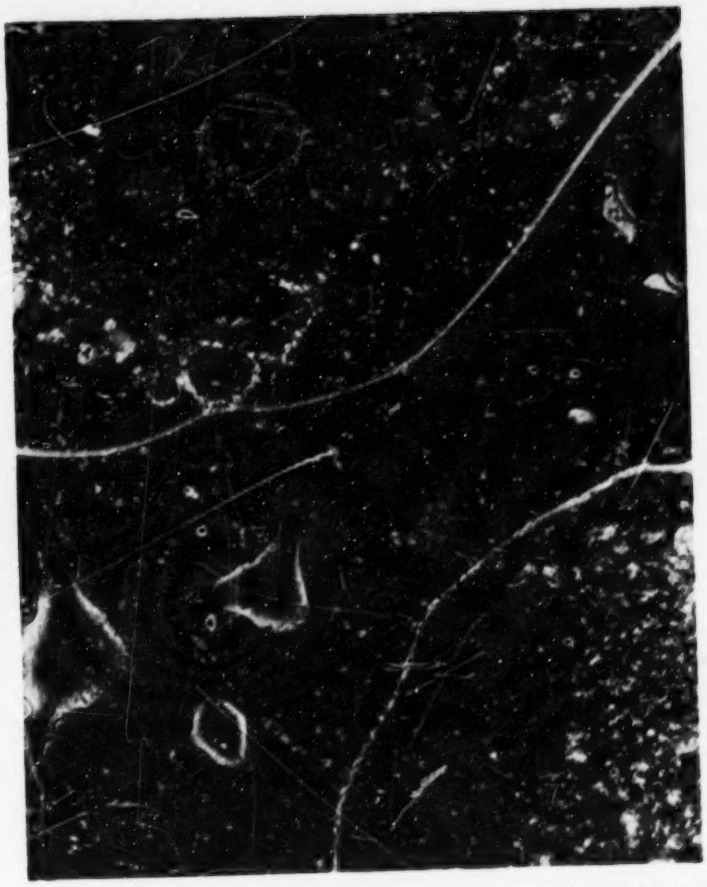

Figure 3. Fluorescent photomicrograph of an oil positive culture.

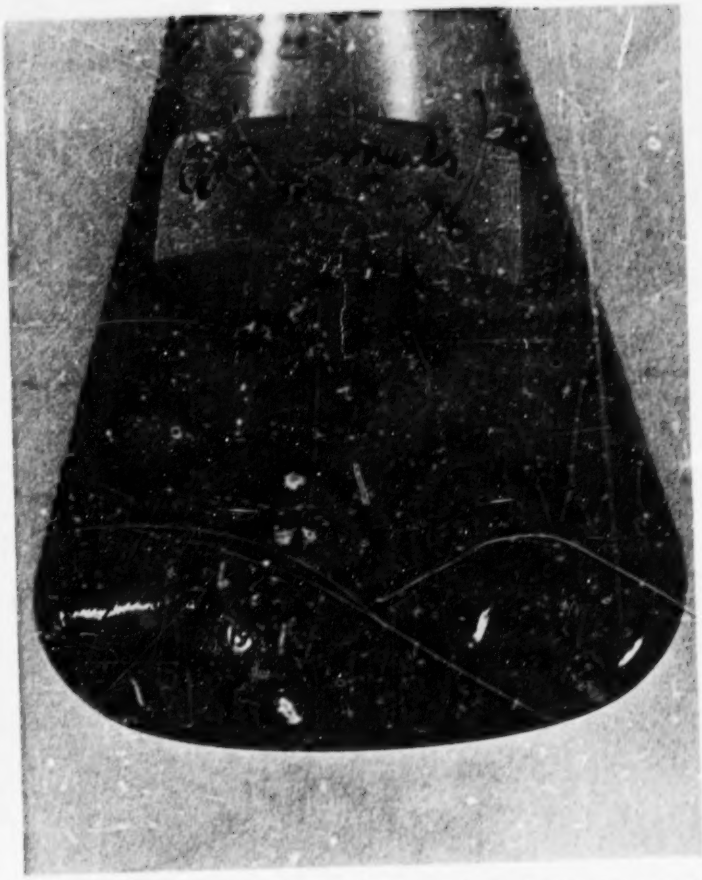

Figure 4. Emulsification of California crude after 72 hours growth of C-63 culture.

TABLE 1. SURFACE TENSION

Sample	Dynes CM^{-1}	
Seawater	71.3	±0.1
Control-E-76 crude on seawater	40.4	1.0
TPLA	44.6	1.0
BHMO	48.2	0.6
OIL RIG	48.1	0.5
C-63	48.8	0.6
SOCLA	37.1	0.4
NOLA	34.7	0.5

1. Measured after 72 hours growth of oil oxidizing microorganisms on 0.1% California crude oil (E-76).

flask. The same California crude after 72 hours growth of an oil positive culture (NOLA) has been degraded to small thin flakes and no longer coats the walls of the container. This is shown in Figure 2.

Another oil positive culture (SOCLA) grows first in the oil phase, leaving a flaky residue, then begins to grow in the water. Figure 3. is a fluorescent photomicrograph of this organism. The bacteria (rods) are in the crude oil residue itself which fluoresces red. Figure 4. shows emulsification of the California crude after 72 hours growth of the C-63 culture. The cells grow in the aqueous phase and emulsify as well as degrade the oil. The production of surfactants is indicated by the inability of the oil to cling to the side of the flask.

Each culture was then allowed to stand undisturbed for two hours at which time the surface tension was determined using a DuNouy tensiometer. For this particular experiment California crude was used, and surface tension was measured after 72 hours growth in enriched seawater containing 0.1 per cent crude oil (Table 1).

These data are difficult to interpret since in some cultures two competing processes are occuring simultaneously–that is, the removal of hydrocarbons by conversion to cell carbon, CO_2, and water soluble intermediate products, decreasing the oil film thickness thus increasing the surface tension, and the production of surfactants which decrease the surface tension.

TPLA, an aqueous phase culture, originally isolated on Louisiana crude did not grow well and had a value only slightly higher than the control. The other three aqueous phase cultures, BHMO, OILRIG, and C-63 had higher values indicating a decrease in surface film thickness (no surface film was visible), but they also produced surfactants as evidenced by the formation of a hydrocarbon-water interface emulsion that was difficult to separate when the cultures were later extracted with benzene.

The two oil positive organisms, NOLA and SOCLA, had lower surface tension values than the control. When these cultures were extracted with benzene, however, the phases separated easily, indicating a lack of surfactant production. These low values may have been due to the flaky residue coating the tensiometer platinum ring.

The crude oil was then extracted with benzene, the solvent evaporated, and a small portion (usually 1 microliter) of the residual oil analyzed on the gas chromatograph. Adamantane, a microbial resistant, cyclic,

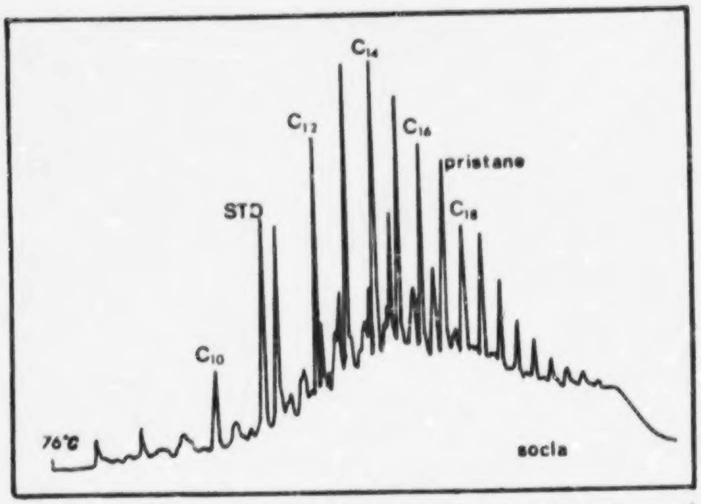

Figure 5. Gas chromatograph trace of undegraded (control) Louisiana crude oil.

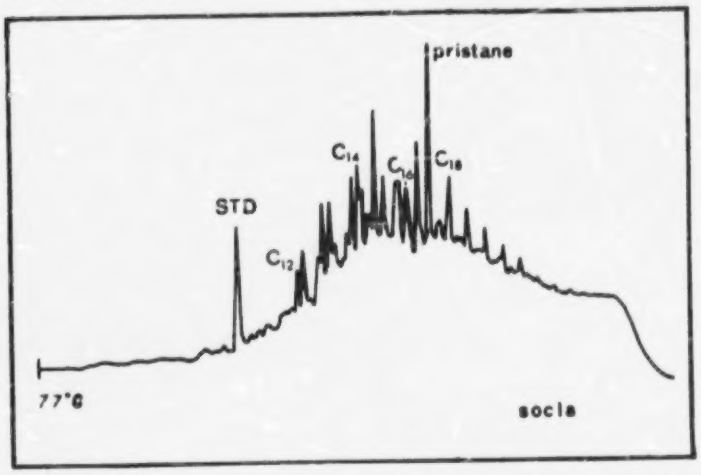

Figure 6. Gas chromatograph trace of Louisiana crude oil (0.1% in 50 ml enriched seawater) after 48 hours degradation by oil-positive microbial culture SOCLA.

highly branched hydrocarbon was added to the original crude oil substrate to serve as an internal standard. However, the peak height of the adamantane was found to fluctuate widely between cultures, type of crude oil used, and length of experiment. This was thought to be due to sublimation effect. Pristane, a branched hydrocarbon found as a natural component of both Louisiana and California crudes, was relatively inert to microbial oxidation during our experimental time periods and thus was used as a standard.

Figures 5 and 6 are chromatograph tracings of undegraded (control) Louisiana crude, and the same oil after being acted on for 48 hours by the SOCLA (oil positive culture). The graphs clearly show the decrease in straight chain paraffins due to continued microbial oxidation. There is a loss in the degraded sample of compounds below C-10, and a marked decrease in the peak heights of the straight chain paraffins from C-10 to C-20.

Figures 7 and 8 show undegraded and degraded California crude (E-76). Results are similar to those of the SOCLA culture on Louisiana crude except for additional peak height decreases in the C-20 to C-25 normal paraffins.

Figure 9 shows changes, resulting from microbial degradation, in peak height ratios, normalized to pristane, in the C-10 to C-19 straight chain paraffinic hydrocarbons. These cultures were grown on Louisiana crude. The TPLA culture significantly decreases the C-10 to C-19 straight chain hydrocarbons within the first 14 hours. The other cultures approach comparable degradation after 60 hours. Only the BHMO culture left significant amounts of C-12 to C-19 normal paraffins undegraded. However, it was very effective in dispersing the oil. One can easily see the decrease in normal paraffin components in the Louisiana crude oil with incubation time.

After gas chromatography procedure on controls and cultures, the residual crude material (corrected for that used in chromatography) was analyzed for total carbon by wet combustion. The oil was mixed with a sulfuric acid-dichromate solution, heated at 50°C for one hour, diluted 1:10 in distilled water and the per cent transmission of the resulting solution measured. This produced, as compared to known controls, the best quantitative method at present for determining rates of oil removal.

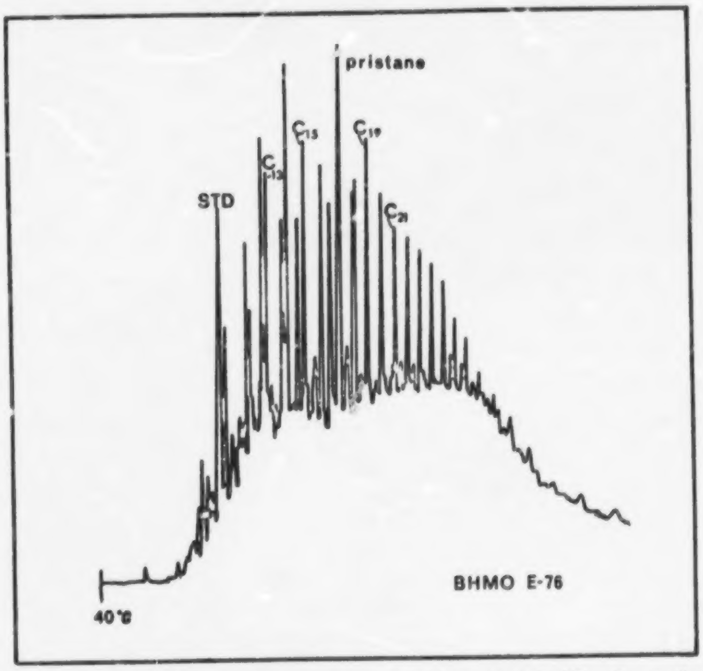

Figure 7. Gas chromatograph trace of undegraded California crude oil (E-76).

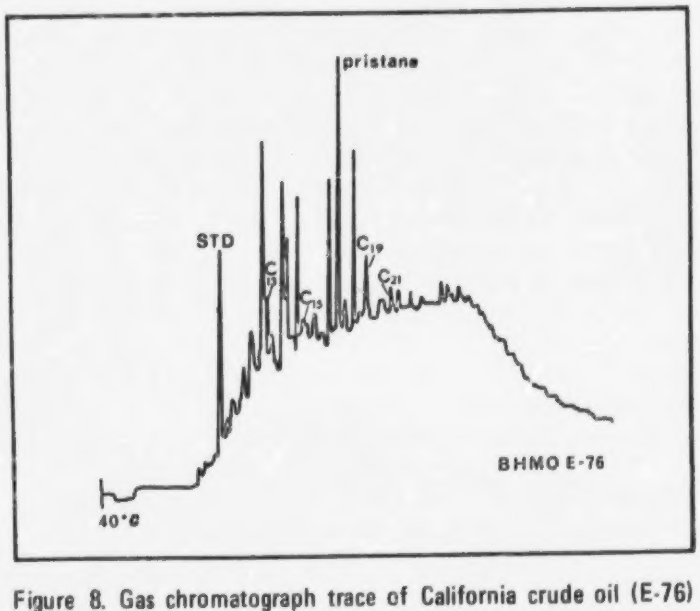

Figure 8. Gas chromatograph trace of California crude oil (E-76) (0.1% in 50 ml enriched seawater) after 72 hours degradation by microbial culture BHMO.

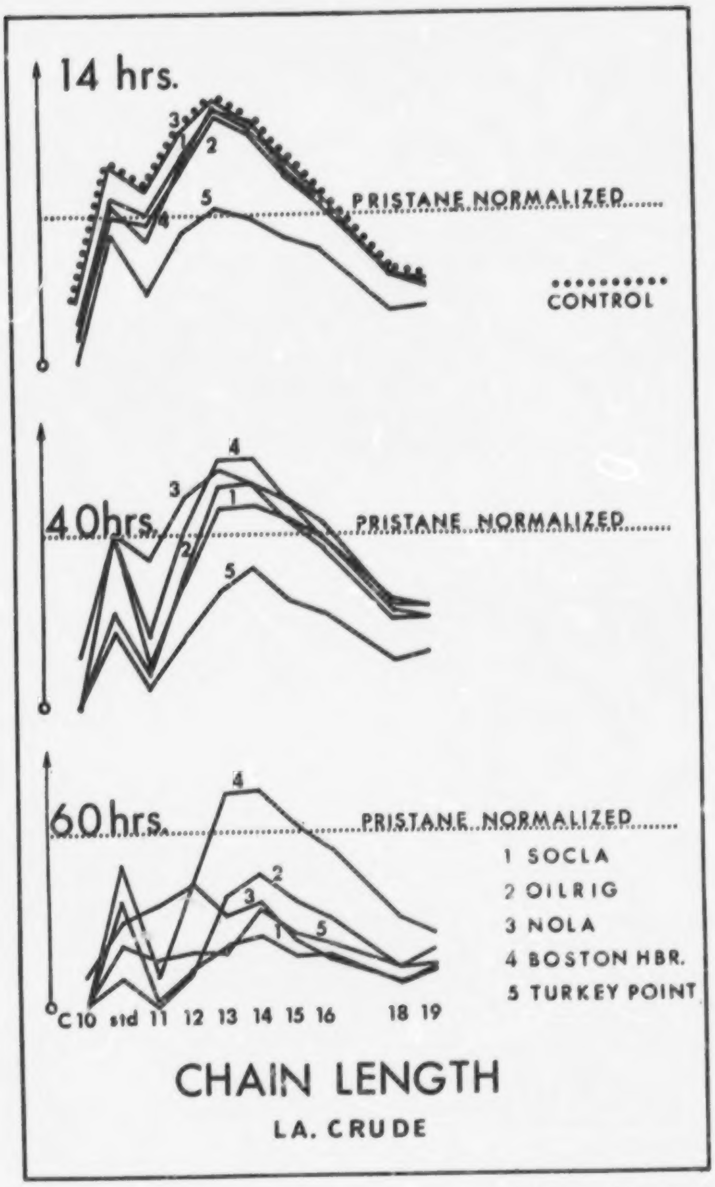

Figure 9. Changes in peak height ratios, normalized to pristance, of straight chain paraffins C-10 to C-19 due to microbial degradation of Louisiana crude oil.

Table 2 shows the per cent of dichromate oxidizable carbon in Louisiana crude oil remaining after 60 hours degradation by five cultures. NOLA (oil positive) has a lag period of approximately 24 hours before it begins to actively degrade the oil. After 60 hours most cultures had degraded from 40 to 50 per cent of the dichromate oxidizable components in the crude oil. These values are in agreement with similar experiments reported by others (4).

TABLE 2. WET COMBUSTION

Percent Louisiana Crude Oil Degraded

Sample	Time (Hours) 14	40	60
SOCLA	13	40	50
NOLA	0	15	35
OIL RIG	13	37	41
TPLA	29	47	55
BHMO	22	32	41

1. Determined by $K_2Cr_2O_7$ oxidation of residual crude oil after benzene extraction.

Conclusion

Fifty mixed cultures of active hydrocarbon degrading marine microorganisms have been isolated. Six of the cultures were studied for their ability to degrade crude oils. Most were shown by gas chromatography to readily oxidize normal paraffins up to C-25. Thirty-five to fifty-five per cent of the dichromate oxidizable crude oil was utilized within sixty hours in enriched seawater. Emulsification of the crude oil occurred in most cultures. A chemostat approach is indicated to determine proper rates of oil removal.

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Kinetics Of Dissipation And Biodegradation Of Crude Oil In Alaska's Cook Inlet

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Abstract

The results of a study to quantitatively define the magnitude of oil pollution problems in Alaska's Cook Inlet are reported. Physical dissipation and biodegration rates were determined and combined with estimates of hydrocarbon input rates to assess the fate of oil in Cook Inlet. The question of accumulation of crude oil components within the Inlet is considered from the above results and by direct analysis. Results indicate that hydrocarbon accumulation is less than our present limits of detection. Cook Inlet flushing is 90 per cent complete in 10 months. Experimental results show that unsupplemented Cook Inlet water effectively degrades Cook Inlet crude, that this biodegradation is essentially complete in the order of a few months, and that the biodegration capacity of Cook Inlet is large. Thus biodegration is more important than physical flushing in removing hydrocarbon pollutants from Cook Inlet. The methods and results are discussed in terms of their applicability to other areas.

Cook Inlet (Figure 1) is a major estuary located in southcentral Alaska. The inlet itself is approximately 150 n miles long and 50 n miles wide at the mouth. The estuary is naturally divided north and south into two regions by the topographic features of the West and East Forelands. Two major extensions exist at the head of the inlet, Turnagain Arm which is 43 n miles long and Knik Arm which is 45 n miles long. The bottom of the inlet is extremely rugged and bottom sediments are sand and gravel. Mud flats exist along the north and west shore. The average depth of the inlet may be taken as 300 feet at the mouth, 120 feet near the forelands, and 60 feet near the head. Knik Arm averages 50 feet for about half its length and then rapidly shallows to a large mud flat. Turnagain Arm shallows within the first 10 n miles to large mud flats cut by many tidal channels.

Tides and tidal currents are large.[1] The mean diurnal tidal range varies from 13.7 feet at the mouth to 29.6 feet at the City of Anchorage on Knik Arm. High velocity tidal currents are associated with these extreme tidal height differences. In the region of the forelands, velocities reach 3.8 knots and elsewhere, above these narrows, maximum velocities are in the range of 2.8 to 3.0 knots. In local areas velocities can be in excess of 5 knots. Large sheets of ice move back and forth with the tides during the three winter months.

Cook Inlet is a multiple-use estuary supporting large commercial fisheries, industrial and shipping usage, and extensive wildlife resources. Salmon, halibut, and crab are the more important commercialized fishery resources. Salmon and clams form the basis of recreational fishing. Additional wildlife resources include seal, beluga whale, ducks, geese, swan, and other waterfowl. Major oil industry related installations in Cook Inlet are shown in Figure 2. Offshore oil and gas wells are located from fifteen offshore platforms concentrated immediately north of the forelands. Underwater pipelines carry the oil to gathering facilities at East Forelands, Granite Point, and West Forelands where co-produced water is removed. From there, most of the oil goes to pipeline terminals for tanker shipment. Kenai Pipeline Terminal is located at East Forelands and the Cook Inlet Pipeline terminal is located at Drift River on the west shore.

Refineries and petrochemical plants are located at East Forelands and include the Standard Oil Refinery, Phillips Liquified Natural Gas Plant, Collier Chemicals Ammonia

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This paper is Contribution No. 61 of the Institute of Marine Science, University of Alaska, College, Alaska.

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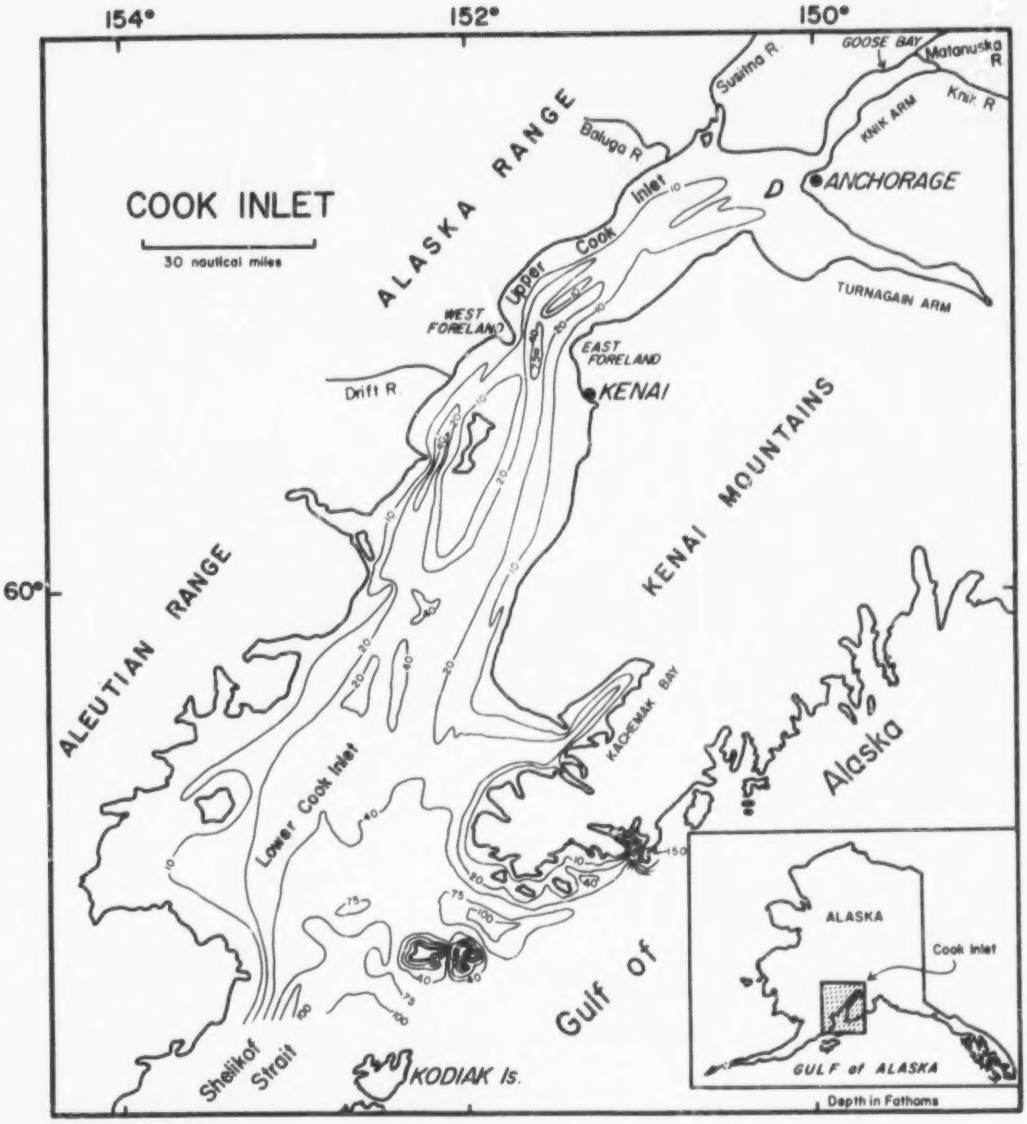
Figure 1.
Map of
Cook Inlet, Alaska.


154°
152°
150°
60°
COOK INLET
30 nautical miles
ALASKA RANGE
Susitna R.
GOOSE BAY
Matanuska R
Knik R
KNIK ARM
Beluga R
Upper Cook Inlet
ANCHORAGE
D
TURNAGAIN ARM
WEST FORELAND
EAST FORELAND
KENAI
Drift R.
KENAI MOUNTAINS
ALEUTIAN RANGE
KACHEMAK BAY
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Gulf of
Shelikof Strait
KODIAK Is.
ALASKA
Cook Inlet
GULF of ALASKA
Depth in Fathoms
10
20
40
75
100
150

Plant, and the recent Tesoro Refinery. The purpose of the present study was to quantitate Cook Inlet oil pollution in a manner that would furnish numbers to guide both industry and government. A secondary purpose was to develop both methods and results on the behavior and effects of petroleum in natural waters that would be of general applicability. Basic to this second point was the hope of a better method of monitoring pollution than the traditional, statistical inference of causes from difficulty measured biological damage. This latter approach is difficult in that continuous biological monitoring must be done wherever a pollution threat exists. More importantly, the questions needed to solve the pollution problem need to be answered with data on the specific mechanisms involved.

Three questions pertinent to oil pollution of natural waters need quantitative answers:

1. Fate of Oil:
   Upon entering the water, where does the oil go, in what concentrations and compositions versus time and place?
2. Toxicity:
   Given the information of 1. what are the specific physical or biochemical toxic mechanisms of damage?
3. Treatment of Spills:
   Based upon firm knowledge of 1. and 2., how should a major spill be treated to minimize damage?

Progress must of necessity be measured in relation to these vigorous goals of ultimate solution to oil pollution. The bulk of the present work is addressed to the first question, the beginning, but the results have implications for topics 2. and 3.

Consider Cook Inlet to be an open system 150 n miles long, 50 n miles wide at the mouth, with a total volume of $1.7 \times (10)^{13}$ ft.^{3} Consider the fate of oil question initially as an oil material balance about the Cook Inlet system. The rate of oil accumulation must equal the rate of input minus the rate of output and minus the rate of consumption thus:

Accumulation = Input - Output - Consumption

We have tried to elucidate all the mechanisms affecting each term of the above equation and tried to measure their corresponding rates.

Results

Input. The input term can be considered to be the unknown for which the equation is to be solved. However, an estimate by independent means is most helpful at this time as a check on the magnitude of the other terms. To estimate the order of magnitude of the accidental input term, data available was obtained from Federal and

State sources for years 1966, 1967, 1968, and 1969 on oil sightings in Cook Inlet gathered on:

1. random flights, and
2. flights following reports by industry and others.[2]

These data were combined with data on the amount of oil per unit areas of slicks (100 gallons/miles,[2] 3 hours old; and 30 gallons/miles,[2] 8 hours old), from measurements made on a large pipeline incident, and from a small experimental spill. Work was done from a Dehaviland Beaver float plane. In the case of the experimental spill, 20 gallons of Cook Inlet crude were poured on the water in the region of the forelands and were followed for a day by measuring and sampling from the air and on the water. The results of combining the above data indicate an input term of 2,000 - 10,000 bbl/year, almost all of it in the form of large, reported accidental incidences. The contribution from random sightings on a yearly basis ranged from 20-300 bbl/yr. The waste water from routine process streams discharged into the inlet from platforms, terminals, gathering facilities, and refineries and petrochemical plants contribute about 7,500 bbl/yr. of oil. This total input of 9,500 - 17,500 bbl/yr. corresponds to approximately 0.03 per cent of the total oil produced or handled in Cook Inlet.

Output. One important output term is due to the physical flushing of the estuary. The Cook Inlet estuary can be classified[3] according to physical circulation deduced from salinity distribution. Surface salinity and temperature distributions (Figures 4 and 5) along with detailed depth profiles presented elsewhere,[4] show that Cook Inlet can be typed as a two-layer flow estuary with intense vertical mixing which approaches a vertically homogeneous estuary with lateral variation due to coriolis force in the region north of Kalgin Island. An overall analysis of mixing in an estuary, in order to estimate the rate of removal of a pollutant introduced into it, is usually done by using fresh water as a tracer. Flushing of an estuary depends on the river input rate and salt water replacement rate due to mixing entrainment. A simple salt balance yields the following expressions assuming steady state:[3,5]

$$R(O) + V_i(S_o) = (R + V_i)\, S_a \tag{1}$$

or

$$V_i = \frac{RS_a}{(S_o - S_a)} \tag{2}$$

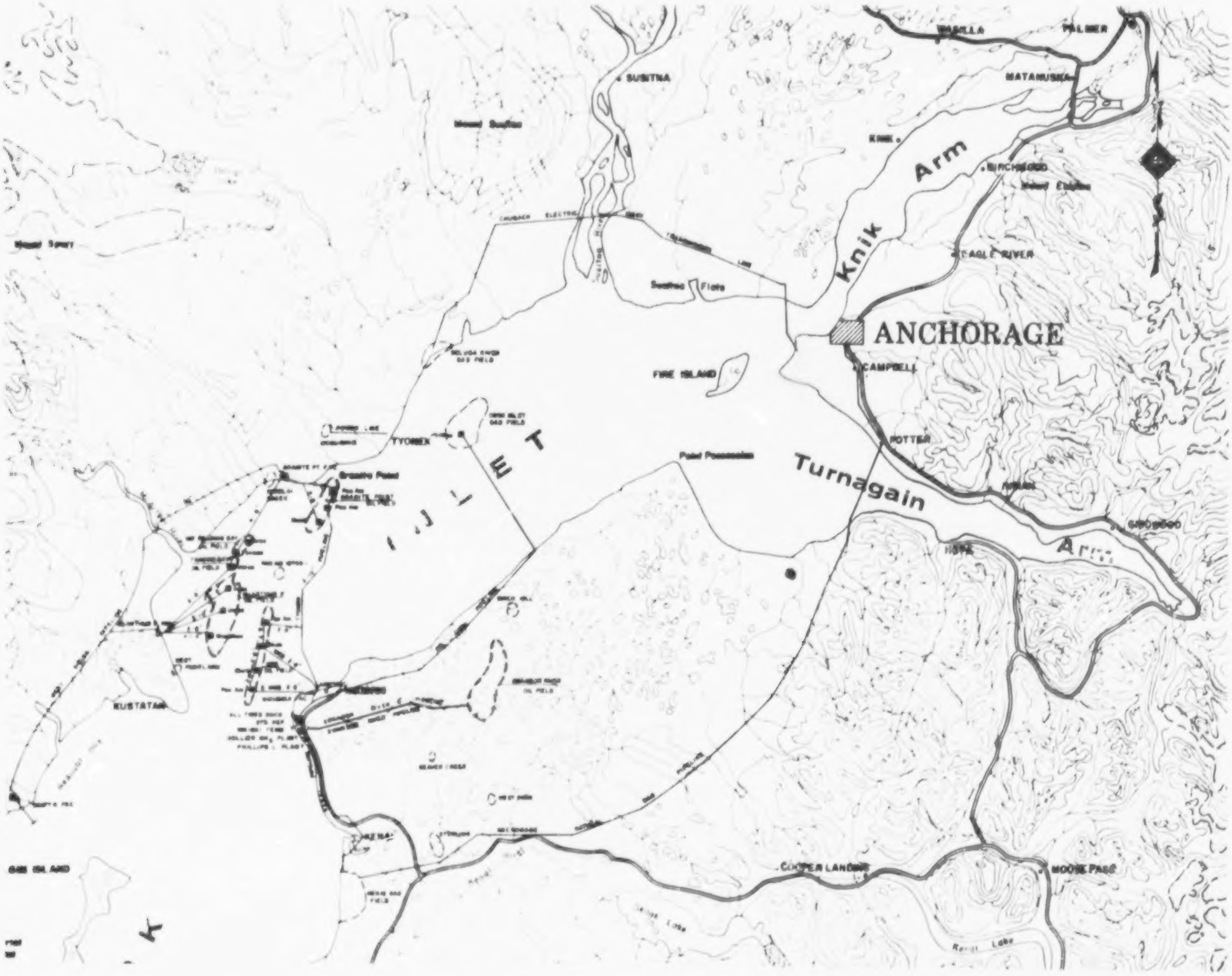

Figure 2. Major oil industry related installations, Cook Inlet, May 1968.

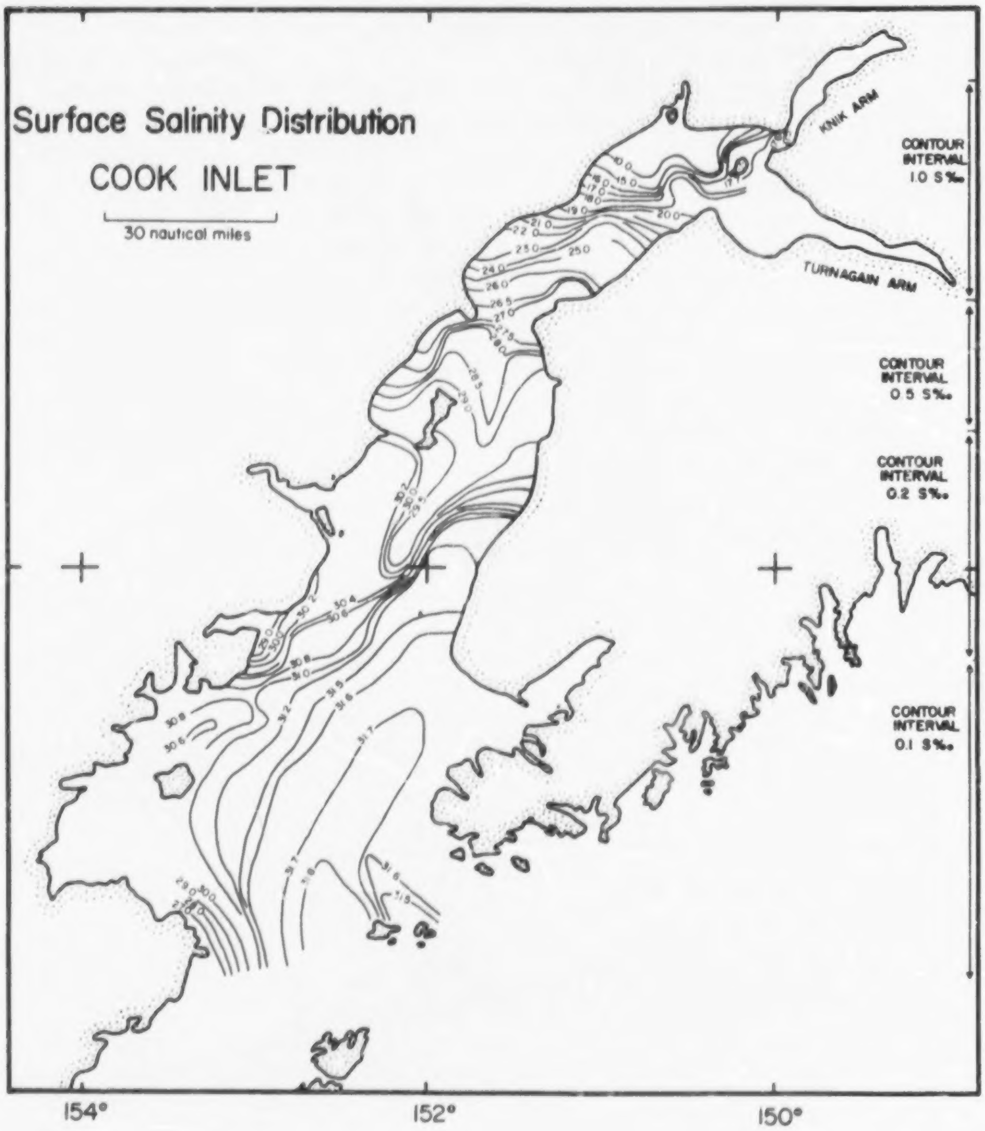

Figure 3.
Surface salinity distribution, Cook Inlet, May 1968.

Where R is the fresh water flow rate into the estuary, S_o is the salinity of the saline source water at the mouth (at depth), V_i is the rate of salt water inflow due to entrainment, and S_a is the average salinity of the estuary. Using June salinity and river flow data[5] values of S_o=32.0 per cent, S_a=29.7 per cent and R=1.02(10)^5 ft.^{3}/sec. were obtained. Using these values in the salt balance equation, the value of V_i=1.32(10)^6 ft.^{3}/sec. is obtained which is equivalent to 4.40 (10)^{13} ft.^{3}/yr for the total input term $(R+V_i)=F$. Winter time river flow rates are only 5 per cent of this June value which would vastly decrease the flusing flow if the salinity distribution were constant. This reduced flushing would be effective for approximately half the year. However, Bowden[3] states that flushing times are not a strong function of seasonal river input variations based upon seasonal analysis of other estuaries. Since in Cook Inlet, tidal turbulence, independent of season, is a major factor in salt transport up the estuary, the V_i term would be expected to remain high. The very limited winter salinity data available also indicate a significant increase as would be expected. Therefore, using the above figures the approximate time for an introduced pollutant to be reduced to 10 per cent of its original concentration by flushing is given by the following expression with V being the total inlet volume:

$$t_{90\%} = \frac{(V)}{(R+V_i)} \ln 10 = 10 \text{ months} \tag{3}$$

Similarly an oil material balance

$$V\frac{dc}{dt} = I - Fc \tag{4}$$

Where I is the yearly input of crude oil and c is the resulting crude oil concentration in the water, results in a steady state crude concentration of 0.82 to 1.5 μg/ℓ based upon yearly inputs of 9,500 to 17,500 bbl/yr. (1 μg/ℓ = 1ppb) Time to reach 90 per cent of the steady state value would be approximately one year, starting from a zero concentration.

Output due to evaporation was determined by field measurements because of the difficulty in simulating air-sea interaction and interfacial emulsion properties in the laboratory. Two sets of measurements were performed with similar results. One involved sampling oil surfacing directly above the Santa Barbara leak and comparing the gas chromatographic spectrum with samples removed from the spill. The second involved sampling a small experimental spill of Cook Inlet crude in Cook Inlet over a period of one day by use of a float plane. Average wind speed throughout the day was 9-12 knots for this experimental spill.

Results of the latter experiment, shown in Figure 5, show that compounds below about C_{12} are significantly reduced in 8 hours. This reduction was presumably chiefly due to evaporation, although solubilization of the lower molecular compounds in the water phase also occurs. From these results, the major fate of gasoline and kerosene fractions is probably evaporation to the atmosphere, with gasoline being essentially gone in 8 hours. For light refined products or for crude oils with significant fractions in this boiling point region (e.g. Cook Inlet crude), this mechanism can thus be important in significantly reducing the water pollution.

Consumption. The major petroleum consumption term is microbial oxidation to CO_2 and H_2O. Field and laboratory observations were made in order to understand the mechanisms and rates involved. Repeated aerial observations of both small experimental spills and large accidental spills indicated the apparent half life of a surface crude oil slick in Cook Inlet was less than a day. Even in the case of a 1,000 bbl. pipeline break, the oil had completely disappeared from the surface in 3-4 days. Laboratory results show that the microflora excrete effective emulsifying agents which help the process considerably. Of course the great turbulence of Cook Inlet, driven by 20-30 foot tides and up to 5 knot currents, is a major factor.

Microorganisms capable of oxidizing crude oil can be found throughout Cook Inlet. Plate counts and most probable number determinations show populations of approximately 10^4 organism/liter with approximately 10 per cent of this population capable of utilizing crude oil. Of interest is the fact that a significant number of oil oxidizing microorganisms enter into the oil phase, rather than remaining in the aqueous phase and working on the surface of oil droplets. Particles of water in oil emulsion, mixed down into the water phase are literally micro-environments, being oxidized by microorganisms existing in both phases. These particles are more dense than sea water due to the presence of oxidized cell material and biomass and oxidized hydrocarbon intermediates. However, moderate turbulence keeps these particles in suspension.

Several microorganisms were isolated and found to use kerosene as the sole source of carbon. Chromatographic analysis indicated that various species selected different components from the hydrocarbons for their carbon and energy sources. Maximum growth rates ranged from 0.02 g cells/ g cells/ hr. in a mineral salts kerosene medium to 0.35 $hr.^{-1}$ on a complete medium.[4] These rates are reduced by a factor of 7 at 5°C, the prevailing summer temperature of Cook Inlet (Figure 4).

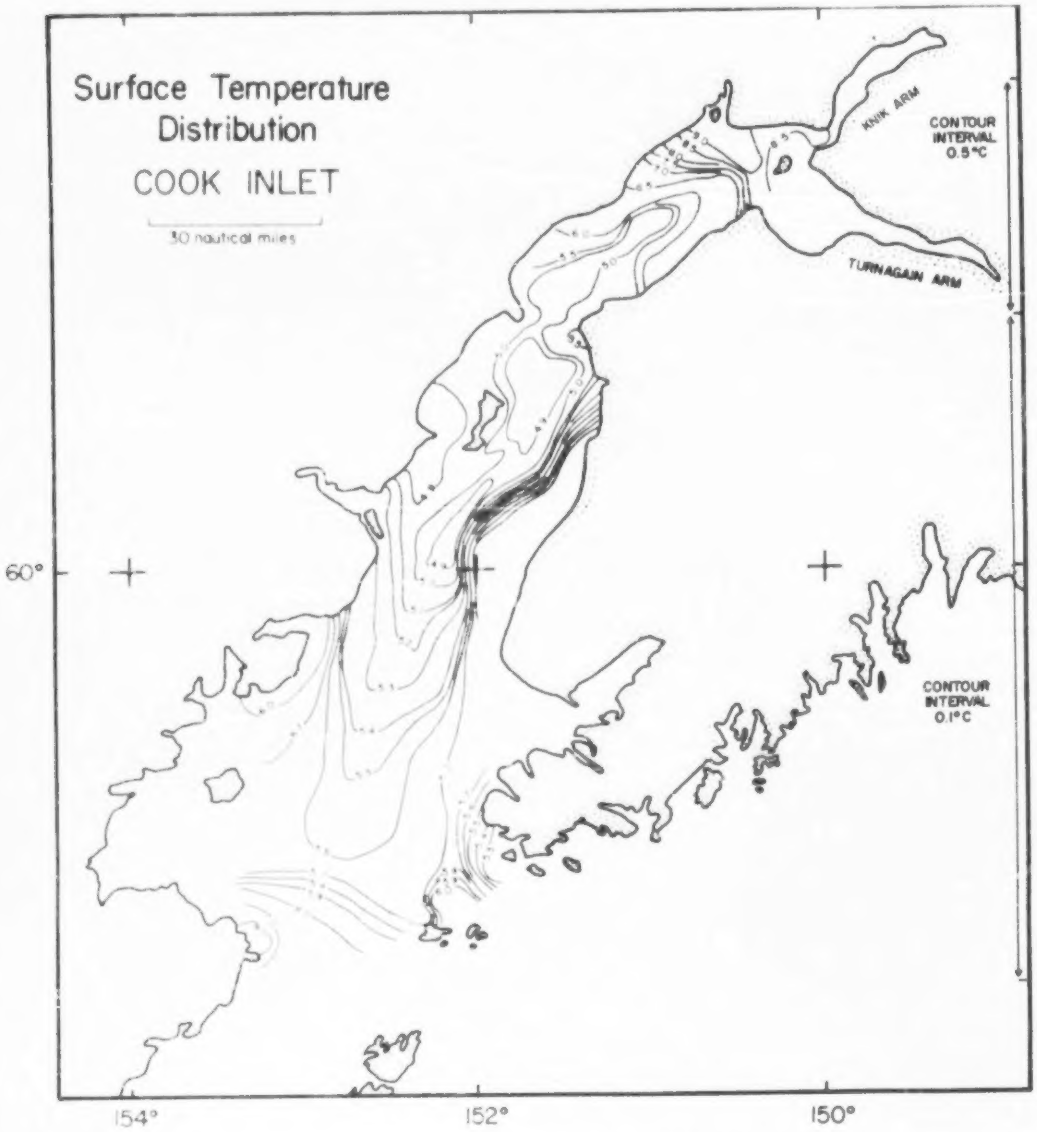

Figure 4.
Surface temperature distribution, Cook Inlet, May 1968.

For dilute populations in the sea, the supply of growth factors is probably adequate, particularly at low temperatures where growth rates are low with respect to diffusion transport. Nitrogen and phosphorous are in excess so that, barring increased inhibitor effectiveness at these low populations by species such as heavy metals, growth rates probably approach those in a complete medium. At this rate a 1000 fold population increase would require 5.7 days and complete oxidation of a 1 mg droplet of biodegradable oil would require 17 days after inoculation by a single bacterium. Populations in sterile bottles filled with Cook Inlet water and supplemented with autoclaved Cook Inlet crude oil were 10^9 per liter after 5 days at 10°C which is in agreement with the above growth rate and initial populations, assuming the success of collisions between the initial population and the oil was extensive during the first day.

Degradation of the heavy crude is probably slower than that of the fraction below C_{25}. Rather heavy artificial slicks confined in a carboy were rich in normal hydrocarbons above this size after two months' incubation with a mixed culture. Degradation of lesser concentrations of crude, 20 mg/1, appeared to be essentially complete after two months at 10°C and less than 5 per cent could be recovered at the end of one year. Artificial slicks on sea water surfaces in stirred carboys were clearly different in inoculated and sterile carboys at the end of three days, and degrading slicks broke up at the end of ten. The presence of silt appeared to have no effect on the process but mixing was extremely important. Slicks in completely unmixed carboys were very stable even when inoculated. Thus it appears that naturally occurring slicks are rapidly inoculated and broken up during the first day after a spill in the very turbulent Cook Inlet. Biodegradation then proceeds first in the micro-environments of the water in oil emulsion, later in the oil drops, and is probably essentially complete in one to two months and certainly before surrounding water is flushed out of the inlet.

Ultraviolet oxidation of crude oil is estimated to be negligible compared to biodegradation and flushing because of the low radiant energy input and the short half life of a thin surface film of oil. However, few data exist on this mechanism.

Accumulation. Independent estimates of the accumulation term were attempted by direct chemical analysis for hydrocarbons in the existing water and sediments of Cook Inlet. Experimental work is also in progress on two other independent methods using ^{14}C radiocarbon[6] and ^{12}C ^{13}C stable carbon isotope[7] analysis of dissolved and particulate organic matter from Cook Inlet. A carbon recovery apparatus[8] based on ultraviolet oxidation of the organic matter in sea water is in use for the ^{14}C measurements. Natural carbon in Cook Inlet and Cook Inlet crude seem to have nicely separated $^{12}C/^{13}C$ ratios. We do not at present have enough data to make conclusions from these latter two experimental results.

Direct chemical analysis for hydrocarbons from water and sediments was by gas chromatography preceded by an extractive concentration step. A considerable body of knowledge on the origin of petroleum and the migration in reservoirs[10-20] shows recent sediment C_{20}-C_{33} n-alkane concentrations to be 10-70 μg/g dry weight. One reference[21] for surface waters shows concentrations from 0.2 to 3.8 μg/l and two sea water samples at less than 0.2 μg/l total C_{20}-C_{33} n-alkanes. Blumer[9] has identified by gas chromatography, the presence of C_{14} to C_{33} straight chain hydrocarbons, branched paraffins at an order of magnitude less concentration, isoprenoid hydrocarbons, and at least two olefinic hydrocarbons (squalene and a polyunsaturated derivative of heneicosane). No concentrations or spectra are given. Thus the knowledge of natural hydrocarbons in aqueous systems is very limited; however, it is known that they are present and that their concentrations are extremely low.

In the present work, four liters of water, sampled with a large volume sampler of glass, stainless, and teflon, was extracted three times with pre-purified n-pentane and the extracts combined to 500 ml. Evaporation at 36°C with a small reflux condenser reduced the volume to approximately 1 ml. Silica gel chromatography[9] was used to isolate saturated hydrocarbons and the isolate in pentane was evaporated to a fraction of a ml and injected into a temperature programmed gas chromatograph equipped with a flame ionization detector. A fifty foot 0.025 inch diameter open tubular capillary column with 5 per cent OV-17 on the wall coating support was used Detection limits as determined by internal standards was of the order of 0.02 μgm/l for individual hydrocarbons in the C_{10}-C_{25} molecular weight range or about 20 μg/l of Cook Inlet crude. Analysis of samples of water and suspended sediments from 70 stations distributed throughout the Inlet showed completed negative results to the detection limits quoted above. Thus these results indicate that the Cook Inlet system is not grossly polluted by hydrocarbons. However, the present detection limits do not allow an independent estimate of the relative effectiveness of flushing and biodegradation. Work is continuing on improving these detection limits by one or two orders of magnitude by eliminating the sample splitter for the open tubular column or by use of conventional columns.[21]

Data on light gas analysis (C_1-C_5) showed indicated possible minute leakage from the reservoir structures; however, the amounts involved are infinitesimal in terms of hydrocarbon pollution. Accumulation of microbiologically fractionated refractory compounds appeared to be negligible and is discussed in C above and elsewhere.[4]

The possible buildup in Cook Inlet of toxic transition metals from crude oil pollution was considered. If the highest value from above for the crude input is assumed and combined with the general ppm concentrations of trace metals in crude, then the steady state level of trace metal concentrations due to oil input is limited by physical flushing to a value three orders of magnitude below natural levels. Thus this danger does not seem to be a real one in Cook Inlet. Also, our biodegradation rates run with Cook Inlet crude, would consider localized concentrations of trace metals effecting these rates.

Discussion

Major effects of accidental spills on the environment of Cook Inlet are not clear. Certainly spills would have little effect on the water chemistry such as carbon, oxygen and nitrogen which are usual indicators of pollution. The more important effects of a large spill might be reduction of the

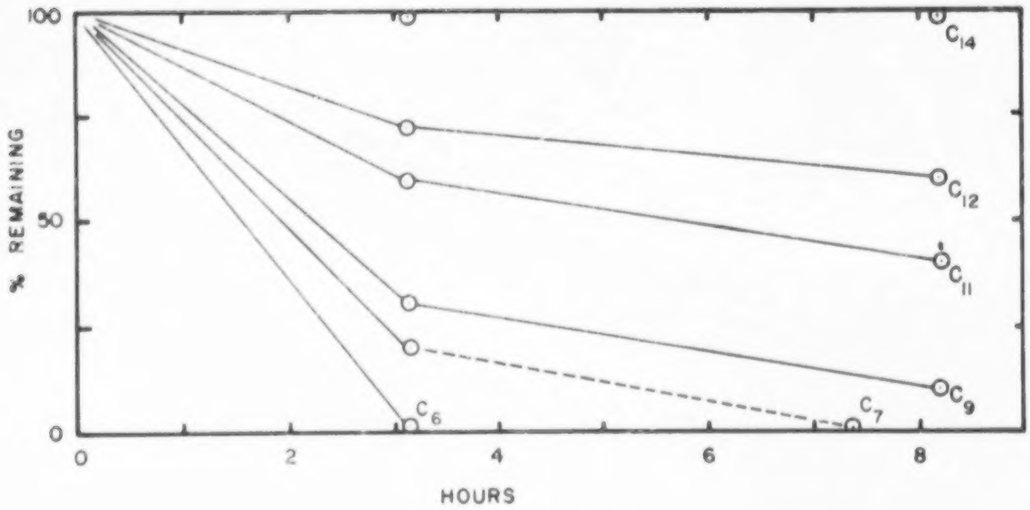

Figure 5.
Evaporative loss of low molecular weight hydrocarbons in an experimental spill of Cook Inlet crude in the forelands regions of Cook Inlet.

aesthetic quality of beaches, fouling of fishermen's gear and oiling of water fowl. Continuous oil slicks on the surface are probably of more concern than similar quantities of oil dispersed below the surface. Only at the surface does oil contribute to the aforementioned problems.

Aside from prevention, no technology exists to substantially minimize damage from a large accident. Recognition of biodegradation as the fastest process in removal of hydrocarbons from Cook Inlet has implications for the treatment of oil spills. For example, detergents might be designed to act in concert with this process.

Given potentially high rates and capacity of the biodegradation mechanism methods of sinking oil spills into the water column may well be practically, as well as ecologically, attractive. The large quantities of Cook Inlet sediment available might be investigated as a type of vehicle, after proper treatment, to do this.

Some of the information gathered here is applicable elsewhere. For example, biodegradation appears to be a significant low temperature process. Lack of mixing is a significant hinderance to this mechanism. Hence, a potential oil spill problem area, such as the Arctic, should be investigated in terms of the physical stability of oil in pack ice and in the comparatively poorly mixed surface waters. The biodegradation mechanism should be assessed under these conditions.

Conclusions

1. Estimated input of petroleum hydrocarbons from accidental spills and effluents is approximately 10,000 to 17,000 barrels per year or approximately 0.03 per cent of the total produced and handled in Cook Inlet.
2. The half life of an oil slick on the surface of Cook Inlet is less than a day.
3. Tide driven turbulence is the chief factor in breaking up oil slicks on the surface of Cook Inlet.
4. Generally, strong tidal currents and their geometry tend to keep oil which has been spilled out in the inlet away from beaches, with the exception of Kalgin Island.
5. A microflora of hydrocarbon oxidizing organisms exists at a concentration of about $10^3/l$ which functions as an inoculum and suggests the present of transient hydrocarbons.
6. Biodegradation of Cook Inlet crude oil in Cook Inlet is essentially complete in one to two months.
7. Tidal and river driven flushing reduces Cook Inlet components within the inlet by 90 per cent in about 10 months.
8. Evaporation effectively removes components smaller than about C_{12} within 8 hours.
9. Accumulated petroleum hydrocarbons in the range C_{10}-C_{25} were below the limits of detection, 0.02 μg/l, in Cook Inlet waters and suspended sediments. Trace transition metals from crude oil were found to be limited by physical flushing to levels three orders of magnitude below natural levels.

Acknowledgements

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Movement Of Oil and Water In Santa Barbara Channel, California

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(Manuscript not available for publication)

Conference Summary

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Summary

The most significant and surprising aspect of this Conference was the fact that eleven hundred people–about three times what had originally been anticipated–came to exchange information on the crucial topic of oil spill prevention and clean-up.

Conservationists, pollution control officials, petroleum industry representatives, university scientists and equipment manufacturers all made a contribution, and all came away with new information and ideas.

One of the most important lessons learned was that while the information exchanged was the most advanced thinking on the subject, there is still a long way to go. The body of knowledge is growing rapidly--but the unknowns still outweigh the knowns.

A sketch of the dimension of the problem was drawn in the opening session by K. E. Biglane of FWPCA. He pointed out that we are approaching a frequency of 10,000 oil spill incidents a year. About two-thirds of them are in port and harbor areas and are generated in routine petroleum transfer operations. And while bigger spills are the ones that make the headlines, it is the smaller more frequent accidents which may, in the long run, place the severest burdens on our ecological systems.

The Conference heard reports on contingency plans–both those developed by the federal government and those developed by the petroleum industry.

Cooperative efforts for spill clean-up have been formally established in 23 U.S. port areas and plans for other cooperatives are being drawn up in an additional 27 areas.

Several federal agencies are conducting broad research programs on the containment, recovery and treatment of oil spills. To date, the American Petroleum Institute has allocated $1¼ million to oil spills cleanup research. This is only a small part of total industry effort. Individual companies, of course, are carrying out extensive research of their own. Government and industry are working closely together to assure that their programs complement one another.

United Kingdom representatives outlined research being carried on there by both the petroleum industry and various Ministries of the Government. The use of chemical dispersants on the Cornish Coast following the *Torrey Canyon* spill caused damage to marine and plant life in the intertidal zone. A number of petroleum industry representatives expressed similar cautions concerning the use of toxic substances in intertidal zones or in shallow areas where harm to marine life–and fish harvest potential–is likely to occur. It was noted, however, that fish catches in the area of the *Torrey Canyon* showed no long-term decrease.

One of the more promising techniques for the dispersion of oil slicks, according to U.K. representatives, is the use of sand slurry sprayed on the slick. Reported on, too, by this group was work done on the burning-off of petroleum as a possible means of disposal from wrecked tankers. The use of booms for containment was also discussed extensively with the general conclusion that they are presently ineffective in any sort of chop or swift current, although they may be of considerable help with smaller spills encountered in calm areas.

Considerable work carried out by the U.S. Coast Guard in regard to parameters for boom design was

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discussed as were research projects being carried out for the Coast Guard on air-mobile equipment for taking petroleum from stranded tankers and for the mechanical containment of spills in open seas.

Chemical and physical additives were discussed at length as were laboratory techniques to evaluate the toxicity of the additives and the effectiveness of various dispersal techniques.

In addition, Navy representatives provided information on the handling of limited oil spills in harbor areas and data on a new approach–the use of a molecular "piston drive" for clearing oil out of inaccessible areas.

Information was provided on how a beach should be cleaned up if it does become oil stained. The most important thing learned was that there is no one acceptable technique. The weather, the temperature, and type of oil, the velocity of the surf, the gradient of the beach and the type of sand all have to be taken into consideration.

Discussed, too, were possible techniques for picking up straw if that material is used as an absorbent. It was stated that agricultural equipment manufacturers are putting some thinking into this problem.

Swift salvage operations by trained personnel were discussed in relation to tanker strandings and collisions. This is an aspect too frequently overlooked in discussions of pollution prevention.

First hand experience of what actually happens with a major spill incident was related by Tom Gaines of Union Oil. This experienced reflection on mobilizing resources, handling the primary problem, and dealing with the huge public interest focused on the Santa Barbara spill was invaluable.

Some solid scientific evaluations of ecological results of both the *Torrey Canyon* and the Santa Barbara incident were discussed. Thankfully, the evidence indicates no serious impairment of marine plant and animal life in either area. However, there is no reason for complacency.

Lastly, work to better understand microbial action on crude oil and petroleum products was reported as well as the development of fundamental theory related to the fate of oil spilled on water.

Research Needs

The conference has made clear the research that is needed.

The primary thrust of any R&D program should be to prevent, minimize, abate, and clean up the consequences of oil spills. Oil spills are awesome in their extent; a start has been made toward preventing, controlling, and cleaning them up. But only a start. What else is needed? Perhaps a page should be taken out of the nuclear power development effort. In that industry, safety considerations are in terms of successful stages of containment, with emphasis on prevention and countermeasures to try to prevent damage to any of the containment schemes considered.

No one technique, system, or piece of equipment is considered to be entirely adequate. Similarly, perhaps what needs to be developed is a large array of physical, chemical and biological means, methods, techniques, devices and hardware that can be used separately or in concert or in a system to prevent, minimize, control, collect, contain, recover, and dispose of oil and hazardous materials pollution. In addition, it is also necessary to assess the short and long-term biological and ecological significance of changes, effects and consequences upon the environment due to oil spills and of any measure taken to combat such pollution.

High priority will still be given to the very large oil spills. Efforts should continue to be directed to provide effective and practical answers to those responsible for implementing programs to prevent and cleanup this class of oil spills. Significant research efforts should also be directed to the non-emergency, day-to-day, chronic problems, associated with small spills, which although less serious on an individual basis, could nevertheless have considerable impact on the affected waters.

Prevention

Because of the high cost and limited effectiveness of clean-up and control methods now available for coping with and minimizing the effect of spills, a high, long-term priority should be placed upon spill prevention. Some methods to be considered include training of terminal crews not only on their equipment but on the consequences of spills; development of equipment designed specifically for spill prevention aspects; and development of navigation procedures, navigation instrumentation, and ship design to include prevention of outflow of oil.

In spite of the best efforts towards prevention, accidents will happen. When an accident occurs, the next area for consideration should be to prevent or minimize discharge of oil to the environment. Included in this are better gelling agents and simple means for application; filling false safety compartments with lightweight sorbents; on-board inflatable sausage-like tanks that can be used to off-load and possibly to serve the double duty of a boom.

Offshore drilling operations will expand as the need for new sources of oil increases. Though it is expected that the industry will continue to upgrade this operation, it may not be possible to completely eliminate accidental spills or sub-surface breaks of the type encountered off the coast of Santa Barbara. Accordingly, it is necessary to develop means for containing the spill in the immediate environs of the drilling rig. These include submerged canopies, mechanical and pneumatic curtain walls, and encapsulation techniques.

Cold Weather Problems

Imaginative schemes and special equipment and materials are needed for combating oil releases in the Arctic environment in relation to development of the North Slope. We need technology developed specifically for dealing with the unique problem of pipeline breaks.

Boom Development

Preventative measures cannot be counted on to be 100 percent effective at all times. Following a release the first line of control of oil is by the use of booms. From the available documentation of the use of booms, they appear to be generally ineffective under relatively limited conditions. It is still necessary to develop an array of booms that can be utilized in the open ocean under reasonable conditions of wind, wave, and current. The Coast Guard is currently evaluating four boom concepts for use in open oceans. Hopefully, these will supply a solution for that environment.

Containment capability in rivers, harbors, estuaries and near shore environments is also needed. These booms have different requirements. They should, among other requirements, be capable of maintaining their relative positions during various tidal changes, be capable of resisting high tidal and river currents, permit unhindered navigation where necessary, require suitable lighting and navigation aids, have ease of handling, and have a high frequency of deployment.

Mechanical Harvesting

We must be able to remove the oil about as rapidly as it is being corralled to prevent its re-escape to the environment. There is a short-term high priority need to develop high rate oil-, oil-emulsion and oil-water harvesting devices and systems for use with booms or on the open water. In response to a recent Request for Proposals by the FWPCA, approximately 50 proposals for harvesting devices were received. Hopefully, with what was exhibited at the conference and with the several concepts to be developed and demonstrated, there may be an answer to this need.

As there are now several oil-water separator systems under study, additional work in this area should have a lower priority pending review of results from the respective projects.

Use of Chemical Additives

Chemical additives include dispersants, gelling agents, burning agents, agglomerates, sinking agents and sorbents, and chemical products purported by their manufacturers to be useful for oil pollution cleanup. It is not feasible for any one agency to test the effectiveness of each product proposed. On the other hand, industry should develop viable and effective means for testing its own products and reporting its effectiveness in terms such that a user of the product can recognize and compare its performance with other similar products for the specific job on hand. This concept, initiated in 1969, in the form of guidelines to test toxicity and effectiveness of dispersants, will be extended to other chemical additives, agglomerating agents, and sorbents.

Analytical & Sampling Techniques

Current methods for in-situ sampling oil and subsequent analysis and reporting are woefully inadequate. Investigations using the same "sample" can obtain different results. Consequently, results are usually inaccurate and cannot be correlated between investigators performing complementary work.

There is a critical need to develop analytical and sampling instrumentation to be used to determine the effectiveness of the numerous devices being tested. The current technique for "eye-balling" the effectiveness of a process is totally unacceptable.

Surveillance Requirements

In many cases a proper enforcement of existing statutes is necessary to implement the result and development of an R&D program, as well as to serve the regulations requiring enforcement.

Spill locations in the open ocean are receiving attention. However, capability must also include quantifying the oil spill so effective countermeasures can be planned. There is also a high priority need to develop systems and techniques to enable a rapid response for control and cleaning of the smaller oil spills in harbors and rivers, where, because of the proximity of commercial and public sources, response time may be critical in spite of the fact that the spill will probably be orders of magnitude smaller than the larger spills in the open ocean which we are gearing up to handle.

New surveillance techniques for cleanup operations are needed. We must have the capability to monitor the extent and quantity of a slick, day and night, and have it read out immediately at the scene headquarters where it can be reflected in a suitable countermeasure plan.

Beach Cleanup

Currently, work is being done on the cleanup of sandy beaches. We must now endeavor to extend this part of the program to include restoration of rocky beaches, marshland, wildlife sanctuaries, and the like.

Fate of Oil

There have been many spills, but we still do not fully understand the fate of the oil in the environments where they have occurred. There are too many suppositions included in the evaluations. Needed is the capability to identify an oil slick from its initial release and to follow it through its many avenues of decay and uptake. The ultimate goal should be to factor the effect of natural forces into the "system" for "cleaning up" the oil spill.

Ecological Effects

Evidence indicates that effect on the ecology can run the full spectrum of maximum to minimal depending, again, upon the species under consideration, the age of the oil, the degree of insult, etc.

A capability must be established to be able to utilize sites of oil spills as field laboratories, as was done at Santa Barbara. In addition, there probably is a need for a rigidly controlled test program.

Information Retrieval and Dissemination

Paralleling the development of hardware techniques, equipment, etc., should be an effort to develop a method for collecting all information, and broadly disseminating it in a form that is useful in both R&D and operations.